

PHYSICAL CHEMISTRY

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A. K. MEE, M.A., B.Sc.

FIFTH EDITION

prepared in collaboration with

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PREFACE

BUNSEN is reported to have said, "Ein Chemiker, der kein Physiker ist, ist gar nichts." (A chemist, who is no physicist, is almost valueless.) If this were true eighty years ago, it is even more true to-day. The co-ordination of physics and chemistry, of which Ostwald laid the foundation, now forms the basis upon which chemistry is built. No one can study chemistry with profit unless he has a knowledge of those physical methods which have raised the subject from being a mere collection of facts to a science with a rational basis.

This book sets out to give an up-to-date outline of the results and methods of Physical Chemistry. Whilst it is not intended to be merely a "crām-book" for examinations, the standard to which it takes the subject is conveniently stated in terms of examinations. The book is suitable for students who are preparing for the General Certificate of Education (Advanced and Scholarship level) and Intermediate Science Examinations of the various Universities for University Scholarships, and for University Degrees up to Pass standard. It is realised of course that the first of these classes will not need to read the whole of the book; the teacher will select the passages to be studied. There is no need to emphasise the value of using one text-book for all the examinations enumerated above. The student gets to know the book, and can easily turn up any particular topic. This does not, of course, imply that the student should not augment his knowledge by reading some of the many monographs on various aspects of the subject; indeed, it is hoped that the reading of this book will stimulate him to read more widely, and to this end a list of books which are recommended for further reading is appended to each chapter.

Many students who take Chemistry in the various Public and University Examinations find this branch of the subject difficult because of their lack of knowledge of Physics. They are mainly those who take Chemistry, Botany and Zoology, and have left their Physics at the matriculation stage. For them this book is specially suited, as pains have been taken to make the Physics and Mathematics as simple as possible. Where any physical concept is introduced which is not likely to have been met with by a student of this standard, it is fully explained. This may have entailed the use of some space, but such treatment is justified by the needs of a large class of students. The mathematics used is of the simplest, consistent with the subject being an exact science. Those reading the book for the first time may find the mathe-

matics of thermodynamics difficult, but the chapters on this branch of the subject need be studied fully only by the more advanced student.

Physical Chemistry naturally begins with the study of the atom. In this matter both Physics and Chemistry are on common ground; but so frequently does the chemist look upon this work as pure Physics, that the student must needs go to a text-book of Physics to learn about it. This necessity has been obviated in this book by commencing with an account of the methods used in deciding the structure of the atom. The knowledge thus gained is applied to the study of chemical combination by the electronic theory of valency. This is one of the most outstanding advances in Physical Chemistry of recent years, and has already brought about great changes in the presentation of the facts of Inorganic Chemistry.

All the topics usually dealt with under the heading of Physical Chemistry will be found in this book. It has been made as up to date as possible by the inclusion of recent work on the theory of complete dissociation, the hydrogen isotope, the physical determination of atomic weights, the extended theory of acids and bases, atomic transmutation, the neutron and positive electron, and other topics. A chapter on Photochemistry is included, and it is hoped that this brief account will be of use to students, as few books of this standard mention the subject. Finally, the methods employed in determining the structure of comparatively simple molecules are outlined. This advance in Physical Chemistry is the logical successor to the unravelling of the structure of the atom, and deserves a chapter in a book of this nature.

A.J.M.

PREFACE TO THE FIFTH EDITION

In this fifth edition the book has been revised and brought up to date. Nearly all the chapters have been extended or rewritten in part. The most important changes are in the sections on thermodynamics: in view of the increasing importance of thermodynamics in chemistry, the scope of these sections has been widened. The student is introduced to the subject at the earliest possible moment, i.e., after the chapter on valency. The convention of signs used in the treatment of thermochemistry has been changed to make it consistent with that used in the rest of thermodynamics. The treatment of valency has been expanded with a fuller development of the theory of molecular orbitals; this has necessitated an extension of the sections on wave mechanics in Chapter III. Surface chemistry, voltaic cells and distillation are among the subjects discussed in more detail than in the previous editions.

While engaged on this revision we have received much help, which we gratefully acknowledge. Mr. J. E. B. Randles, Dr. G. A. Gilbert and Dr. G. M. Burnett, all of Birmingham University, suggested the lines along which the revision should be made. Our thanks are due to the following, who gave advice on particular points: Dr. E. M. Philbin and Mr. F. T. Riley, M.Sc. (of University College, Dublin); Dr. N. Porter and Mr. F. O'Foghludha, M.Sc. (lately of University College, Dublin) and Mr. H. P. Hutchison, M.A. (of Trinity College, Dublin). One of us also wishes to acknowledge the constant counsel and encouragement which his father, Professor T. S. Wheeler, D.Sc., and his wife, Mrs. M. Wheeler, B.Sc., have given him throughout the work.

November, 1954.

A. J. MEE,
D. M. S. WHEELER.

A NOTE ON THE REPRINT (1956) OF THE FIFTH EDITION

In this reprint, a number of corrections have been made, and the "Suggestions for Further Reading" have been revised and brought up-to-date throughout.

ACKNOWLEDGMENTS

I most gratefully acknowledge the help of the many sources I have used in the preparation of this book. It is impossible to mention all of them, as every book on the subject that I have read has left its impression upon my memory. All the books mentioned at the end of each chapter have been consulted. I must, however, mention the following, which have been particularly useful. Dr. J. Newton Friend's *Text-book of Physical Chemistry*, Volume I. (Griffin), has been frequently consulted on the properties of liquids, and other points, and has provided me with considerable amount of data for the compilation of some of the tables. *A Treatise on Physical Chemistry* (Macmillan), edited by H. S. Taylor, has proved very useful on a great variety of topics. J. W. Mellor's *Comprehensive Treatise on Inorganic Chemistry*, Volume I. (Longmans), was consulted in connection with Chapter I., and particularly on the history of the liquefaction of gases. Professor S. Sugden's *The Parachor and Valency* (Routledge) gave me considerable help on the subject of atomic spectra, and many of the figures used in the tables of Chapter III. have been derived from this source. It also provided me with the greater part of my information on the Parachor, and the theory of singlet linkages. Professor N. V. Sidgwick's books, *The Electronic Theory of Valency* (Oxford) and *The Covalent Link in Chemistry* (Cornell University Press), have been most valuable in connection with Chapters IV. and XX. respectively. These books should be known by every student of Chemistry. Dr. Eggert's *Lehrbuch der Physikalischen Chemie*, which has now been translated by Dr. S. J. Gregg (Constable), has proved of very great value on many points, and particularly on Photochemistry. I have adopted Dr. Eggert's method of dealing with this subject in Chapter XIX. The *Annual Reports of the Progress of Chemistry* issued by the Chemical Society have been used freely.

The following have kindly given their permission to reproduce diagrams, tables, etc.:-

Professor E. K. Rideal and the Chemical Society, for Plate II., from the *Annual Reports of the Progress of Chemistry*, 1931, p. 322.

Professor N. V. Sidgwick and the Cornell University Press, for Tables XXVIII, XXIX, CVIII, CIX, CX, from *The Covalent Link in Chemistry*.

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Dr. J. Newton Friend and Messrs. Charles Griffin & Co. Ltd., for the use of data in Chapter IX, and Table LXI, from Dr. Friend's *Text-book of Physical Chemistry*, Volume I.

The publishers have allowed me to use certain blocks of illustrations appearing in other of their books.

I must tender my most sincere thanks to my Publisher's Science Editor, who kindly read the work in the manuscript stage, and pointed out numerous improvements. Without his help the book would have been much impoverished. He has also read the proofs, and supervised the preparation of the blocks. I am also very grateful to Dr. L. A. Woodward, who read the work in manuscript and gave many valuable criticisms and suggestions. I have made considerable use of the Library of the Chemical Society, and my best thanks are due to the Librarian, Mr. F. W. Clifford, and the Staff for the help they have always been ready to give.

Finally, the Publishers have done all in their power to make the work entailed in the preparation of a book like this as light as possible for the author, and have always sought to carry out my wishes to the smallest detail.

A.J.M.



ABBREVIATIONS

The abbreviations used throughout this book are those adopted by the Chemical Society in the *Journal*, with the exception of the abbreviation for *gramme*, which is given as *gm.*

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PHYSICAL CHEMISTRY

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LAWS OF CHEMICAL COMBINATION

1. **The Law of Conservation of Matter.**—This law, which is the basis of all quantitative work in chemistry, was first stated by Lavoisier in 1774, although the belief in its truth was current much earlier amongst the Greek philosophers.

The law states that *the total amount of matter in the universe is unaltered, whatever changes take place in its distribution.* The Greeks merely gave this as an opinion, or a belief; their views were not founded on any experiment. Lavoisier, however, came to his conclusion as the result of experiment, and he stated the law in the words: "Nothing can be created, and in every process there is just as much substance present before and after the process has taken place. There is only a change in the form of the matter."

Experimental proof of the Law of Conservation of Matter is difficult. By many chemists the truth of the law was regarded as self-evident, since so much quantitative work had been based on it, and it had always turned out correct within the limits of experimental error. The law was subjected to an exhaustive test by Heydweiller (1901) and by Landolt, whose results were published in 1906.

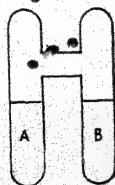


FIG. 1.—
Landolt's
Tube.

It is clear that to test the law, reactions must be carried out in sealed tubes so that none of the products of the reaction escape. Heydweiller found slight losses in weight when reactions were carried out under these conditions, and Landolt set to work to discover to what these losses were due. The simplest form of apparatus employed by him was an H-tube, as shown in Fig. 1, in which the two reactants could be placed in either leg. On inverting the tube, the two substances mixed and reaction took place. If the Law of Conservation of Matter is valid, there should be no difference in the weight of the tube before and after the mixing.

Fifteen different reactions were used, amongst which were the following:—

- (1) Silver sulphate solution in one limb, and ferrous sulphate in the other; on mixing metallic silver was deposited.

- (2) Hydriodic acid and iodic acid, which on mixing gave iodine.
- (3) Sodium sulphite and iodine, which reacted giving sodium iodide and sodium sulphate.
- (4) Potassium hydroxide solution and chloral hydrate, which gave an emulsion of chloroform.

In carrying out an experiment, one tube was counterbalanced against another exactly similar tube. One tube was then inverted, replaced on the balance, and the change in weight noted. The other tube was then inverted, and replaced on the balance, and the change in weight again found. The process was repeated several times, and in almost every case a diminution in weight was observed.

These losses in weight were found to be due to: (a) a slight heat evolution in the reaction which removed some of the moisture which is always present on a glass surface; it took some time for this moisture to return; (b) the heat evolution caused a slight expansion of the vessel, which did not regain its original volume at once. This change in volume caused a change in the upthrust due to the air.

Both these effects would tend to reduce the weight or apparent weight of the containing vessel, giving rise to the apparent loss in weight. It has been shown that, for gaseous reactions, a loss in weight may be occasioned by the permeability of the glass vessel to certain gases. When the surface is coated with paraffin wax, this effect is eliminated.

The two effects mentioned above could be eliminated if the reaction vessel were allowed to stand long enough after the reaction had taken place, and Landolt found that when this was done the original weight was regained to within 1 part in 10,000,000, an error quite within the limits of the experiment. For these reactions, then, the law may be taken as valid.

It should be noted, however, that all the reactions studied take place quietly. There is no great evolution of light or heat. The difficulties encountered in the study of vigorous reactions, with a view to proving that the Law of Conservation of Matter holds for them, are so great, that it is not known whether they do obey the law. Our modern idea of radiation and matter leads to the view that they would not obey it. The emission of radiation, such as light and heat, is accompanied by a loss of mass, which is equal to $\frac{E}{c^2}$, where E is the energy radiated and c the velocity of light. The sun, which is continually radiating, is all the time losing part of its matter. Actually, in all chemical reactions, radiation of some sort is emitted, and consequently the law of conservation of matter can no longer be regarded as an exact law. In ordinary work, however, the amount of radiation emitted is so small as to make any correction in the application of the law quite negligible, although in the

most energetic reactions a change of 1 part in 10^8 might be found. It is interesting to note that it is the conversion of mass into energy that takes place when atomic energy is released (§ 47).

There is little doubt that a true conservation of mass and energy, taken together, does exist.

2. The Law of Constant Proportions.—Proust, as a result of his analyses of compounds, was able, in 1799, to make the generalisation that *"when combination takes place between elements, it is in definite proportions by weight, so that the composition of a pure chemical compound is independent of the method by which it is prepared"*.

This Law, which seems to us self-evident, actually proved to be the centre of a controversy at the beginning of the nineteenth century, between Proust, and the French chemist Berthollet. The latter believed that the composition of a compound was variable, and supported this view by experimental evidence, which however, as Proust was able to show, did not actually amount to any violation of the law. Berthollet said that when lead is heated in air it gradually takes up oxygen, and its colour changes from grey, through yellow to red. There was thus a large number of compounds of lead and oxygen, but no definite proportion of lead and oxygen in them, for the colour changed insensibly from one to the other. Proust was able to show that actually there was a series of oxides of lead, each of which has a fixed and definite composition, and that the colour changes gradually when lead takes up oxygen from the air because the relative proportions of these different oxides are changing.

Berthollet also stated that when mercury dissolves in nitric acid, it takes up the acid in various proportions continuously from a minimum amount, when the mercury is converted into a mercurous salt, to a maximum, when it gives a mercuric salt. Proust showed that there were only two mercury nitrates, a mercurous and a mercuric salt, and that the intermediate substances were merely mixtures of these two.

Numerous other objections were raised by Berthollet, whose one aim at this time seems to have been to overthrow this Law by every means in his power. In every case, however, Proust was able to bring forward evidence in favour of the Law, although this was often a difficult matter. If this controversy was bitter, it did at least promote chemical investigation, and a great increase in chemical knowledge was made at this time largely as a result of it.

The Law has been proved within the limits of experimental error by the work of Stas, who prepared compounds in several different ways, and showed that their composition was the same to within 1 part in 100,000.

No error in any quantitative analysis has been traced to a failure of the Law, so that, although it has not been directly verified for all substances, a task of such magnitude that it could not be completed,

this indirect evidence places its accuracy, as an experimental law, quite beyond doubt.

The converse of the Law of Constant Proportions is not true. If it is found that two compounds have the same composition by weight, it does not necessarily follow that they are one and the same substance. This is due to the existence of isomerides, *i.e.*, substances possessing identity of chemical composition, yet having different properties. A well-known example of this is the isomerism shown by many organic

substances, such as urea, $\text{CO} \begin{array}{c} \diagup \text{NH}_2 \\ \diagdown \text{NH}_2 \end{array}$, and ammonium cyanate, NH_4CNO .

Both these substances have the same molecular formula, $\text{N}_2\text{H}_4\text{CO}$, and yet they are entirely different in their properties. Ethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$, and butyl alcohol, $\text{C}_4\text{H}_9\text{OH}$, are further examples of isomerides. Chemical composition does not therefore uniquely determine a chemical compound.

It should also be noted that it is possible to find two or more definite chemical compounds with identical *chemical* properties, yet differing in *physical* properties and in chemical composition. Thus, lead chloride prepared from metallic lead which has had its origin in the disintegration of uranium minerals, differs in composition from that prepared from lead from thorium minerals. It has identical properties, but different composition. The reason for the difference lies in the fact that the lead from the two sources differs in atomic weight. The atomic weight of ordinary lead is 207.2, whilst that from certain radioactive sources is 208. It is clear that the lead chloride prepared from each of these specimens will have different compositions, although no outward chemical difference can be discovered between them. Actually almost every element is made up of a mixture of atoms of different atomic weights (§ 38). Although these atoms differ as regards weight they do not generally differ at all chemically, and so chemical tests fail to distinguish between them. Such atoms are called *isotopes*. Chlorine gas, as ordinarily prepared, is a mixture of atoms of atomic weights 35 and 37. If these were separated, and then combined with sodium, they would both form common salt, which would give all the chemical tests for this compound, and both specimens would be chemically indistinguishable from each other. Yet it is clear they would not have the same composition. In practice the ordinary elements prepared in the laboratory always contain the same isotopes in the same proportions, and so compounds always have the same composition, whenever and however they are prepared. In order that the Law may be applied, it is necessary to distinguish carefully between compounds formed from different isotopes.

3. The Law of Multiple Proportions.—The Law was stated by Dalton in 1803, and may be put as follows:—

When two elements *A* and *B* combine to form more than one compound, the weights of *A* which combine with a fixed weight of *B*, are in the proportion of small whole numbers.

There is little doubt that Dalton had been working on the atomic theory, and saw that some such law must necessarily be true (§ 9). He found in his experiments on the hydrocarbons marsh gas (methane) and olefiant gas (ethylene), and on the oxides of carbon, some experimental evidence for this view. It is certain that no man of science without an idea of what result to expect would have propounded the Law of Multiple Proportions from the numerical results of Dalton's experiments. The experiments were very crude, and the results far from accurate. Only a person who expected the Law to be true would be able to see the truth of it from Dalton's figures.

Numerous experiments since, however, have shown the truth of the Law. Analyses by Berzelius were considerably more accurate than those of Dalton and provided sufficient experimental evidence. The analysis of three of the oxides of nitrogen has been carried out by different observers and the results are given below:—

Nitrous oxide (Guye and Bogdan, 1904), $N : O = 1.75100 : 1$.

Nitric oxide (Gray, 1905), $N : O = 0.87563 : 1$.

Nitrogen tetroxide (Guye and Drouguine, 1910), $N : O = 0.43782 : 1$.

The numbers expressing the amount of nitrogen combining with 1 part of oxygen are in the proportion,

$$1.75100 : 0.87563 : 0.43782,$$

$$3.9994 : 2 : 1,$$

$$4 : 2 : 1.$$

Similar remarks apply concerning the exactness of this Law as were made regarding that of the Law of Constant Proportions. The existence of isotopes causes similar discrepancies here, unless the same isotope or mixture of isotopes is used throughout the preparation of a series of compounds. This difficulty is only likely to arise with compounds of hydrogen (§ 43, 44) and possibly lead.

4. The Law of Equivalent Proportions, and the Law of Reciprocal Proportions.—The fact that combination between substances takes place between definite weights of them appears to have been recognised by some of the alchemists, particularly by one Al Jildaki, who lived in the fourteenth century. Cavendish, however, was the first to recognise that substances combined together in the proportion of their equivalent weights. Cavendish (1766) first mentioned the word equivalent when dealing with the neutralisation of lime by an acid. He found the weight of potash which would combine with a given weight of acid, and the

weight of lime which would neutralise the same weight of acid. He said that these two weights were equivalent.

The first to note the relationship was Richter in 1792-94. He enunciated the Law of Reciprocal Proportions, which is a special case of the more general Law of Equivalent Proportions. The Law of Reciprocal Proportions states that "*the weights of two or more substances which separately react chemically with identical weights of a third are also the weights which react with each other, or simple multiples of them*".

The following example may be taken to illustrate the Law—

(1) Sodium combines with hydrogen, forming sodium hydride; 23 gms. of sodium combine with 1 gm. of hydrogen.

(2) Sodium combines with oxygen to form sodium oxide; 23 gms. of sodium combine with 8 gms. of oxygen.

(3) Hydrogen combines with oxygen to form water; 1 gm. of hydrogen combines with 8 gms. of oxygen.

Here there are two substances (they happen to be elements in this case) combining with the same weight of a third. If the Law of Reciprocal Proportions is correct it would be expected that the weights of the two elements would be those in which they would combine with each other, and that is indeed the case.

It will be seen that as it stands this Law is of limited applicability, for there are comparatively few substances which, combining with a third, will combine with each other. The fact that they do both combine with the third element means that they must be similar in nature, and combination between similar substances is not to be expected.

The Law could, however, be applied through a chain of substances, and in this way we should arrive at a series of numbers which express the weights with which the different elements would combine with each other. These weights are known as the equivalents of the elements or compounds.

It was formerly usual to take hydrogen as the standard element, because no element was known which had a smaller equivalent; but for various reasons to be stated later, it is now customary to take oxygen as the standard (§ 5).

The *equivalent* of a substance is therefore defined as the *weight of it which will combine with or displace 8 parts by weight of oxygen*.

The Law of Equivalents states that *substances combine together in the ratio of their equivalents*.

The most recent values for the equivalents of hydrogen, chlorine, and silver are 1.0078, 35.457 and 107.880 respectively. These numbers are of great importance as they are fundamental for the determination of other equivalents. It is not always possible to make an element combine with hydrogen, or even with oxygen, but there are few elements which will not combine with chlorine. Since the equivalent of chlorine, referred to oxygen, is known, it is possible to find the equivalent of a substance

by analysing its compound with chlorine. This method, of course, makes use of the Law of Equivalents.

The equivalents of most elements are based on the equivalent of silver, since the chlorides of most elements can be prepared in pure condition, and chlorine can be determined as silver chloride with great accuracy.

5. The Oxygen Standard.—Dalton chose the atom of hydrogen as the standard upon which to base the atomic weights (§ 11) of the other elements. He did this because the hydrogen atom was the lightest.

It so happened that the atomic weights of many other elements determined on this standard came out to be very nearly whole numbers. The number of them which did so was much greater than that indicated by probability, and so Prout, who, by the way, was one of the pioneers of physiological chemistry, considered that they *ought* to be whole numbers. So he put forward his famous hypothesis that the atomic weights of all elements are multiples of those of hydrogen. This gave even more strength to the view that hydrogen should be taken as the standard.

If Prout's hypothesis were correct, it was considered that it ought to be possible to prove by experiment that the atomic weights of all elements were whole numbers and not merely *nearly* whole numbers, but all attempts to bring the elements into this scheme failed. The elements copper and chlorine, with atomic weights 63.57 and 35.46 respectively, proved particularly recalcitrant in this respect. The inability of the theory to cover these cases proved its downfall. There was, however, much more truth in Prout's hypothesis than was at this time imagined, and in the light of the modern view of atomic structure it has again come into its own. That is another story, and must be taken up in the next chapter (§ 38, 40).

For practical purposes it was found convenient to take oxygen with the value 16.000 as the standard of atomic weights. The reasons for this step were:—

(1) It is much more easy to obtain compounds of elements with oxygen than with hydrogen, particularly in the case of the metals. At the time when atomic weights were being determined with accuracy, the preparation and analysis of hydrides was a difficult matter. As it was, on the basis of hydrogen = 1, the atomic weights of elements frequently had to be determined with oxygen as an intermediary, and this meant that every time the atomic weight of oxygen was redetermined, many other atomic weights had to be recalculated. With the atomic weight of oxygen fixed, this would be unnecessary.

(2) The atom of hydrogen is very light, and in making comparisons experimental errors are magnified.

At the time when this work was done nothing was known of isotopes, but it has been found that the masses of isotopes come out to be more nearly whole numbers on the oxygen scale. It is now known that oxygen

itself is a mixture of isotopes of masses 16, 17 and 18, the proportion of the last two being very small. For chemical purposes the naturally occurring mixture is taken as the standard, but the isotope of mass 16, written ^{16}O , is the standard used in the mass spectrograph method for determining atomic weights. In this method the proportions of the isotopes of different masses in the element are determined, and the atomic weight is calculated from these proportions (§ 41). According to the most recent determinations the ratio of a mass on the standard $^{16}\text{O} = 16$ to that on the standard $\text{O} = 16$ is 1.00027 ± 0.00002 to 1.

The discovery of the hydrogen isotope, ^2H , is also of importance in this connection (§ 43).

6. The Determination of Equivalents.—The accurate determination of equivalents is a matter of great importance, since the atomic weight of an element is nearly always derived from this figure. If the atomic weight of the element on the hydrogen scale is a , and the valency is v , one atom of the element combines with v atoms of hydrogen. But, one atom of the element weighs a units, compared with hydrogen. Hence a grams of the element combine with v grams of hydrogen. The equivalent

is thus, $\frac{a}{v}$. The atomic weight of an element and its equivalent are therefore connected by the relationship,

$$\text{equivalent} \times \text{valency} = \text{atomic weight.}$$

The atomic weight is thus always some simple multiple of the equivalent. Although this statement has been deduced using the definition of atomic weight on the hydrogen scale, the student will find no difficulty in transferring the argument to the oxygen scale.

During last century the most accurate work in the determination of equivalents was done by Stas, the master of quantitative analysis. Stas commenced work by studying the action of heat on potassium chlorate. He found the loss in weight that took place when a given weight of potassium chlorate was heated until it gave off no more oxygen. He knew that the compound contained six equivalents of oxygen, so he could determine the equivalent of potassium chloride. He found this to be 74.59 (equivalent of $\text{O} = 8$). By finding the weight of silver chloride precipitated by a given weight of potassium chloride he found the equivalent of silver chloride to be 143.37. The combination of a known weight of silver with chlorine gave him the equivalent of silver, 107.93. Knowing this, he obtained from his other figures the values for potassium and chlorine.

The results of his analyses were extraordinarily accurate, but unfortunately there were two systematic errors. The first was due to the fact that the potassium chlorate contained a small quantity of chloride, and the second to the fact that a small quantity of potassium chloride is always carried down by silver chloride when precipitated by silver

nitrate, and this impurity cannot be removed by washing. The work of Edgar on the direct determination of the equivalent of chlorine showed the existence of this error.

Some examples of the extreme care which has to be taken to obtain an accurate value for the equivalent will be given later when we consider some of the classical experiments that have been carried out, with this end in view (§ 13).

The determination of atomic weights and of equivalents is, however, fast becoming the task of the physicist rather than of the chemist, for results of as great a degree of accuracy can be obtained by physical methods as by chemical ones. This will be more fully understood after reading the next chapter (§ 41).

It will be of value to summarise, at this point, the simpler methods that are available in the laboratory for the determination of equivalents. Although these yield results of only moderate accuracy, they form the nucleus of the more elaborate methods.

(1) The determination of the volume of hydrogen that is evolved by the use of a given weight of metal when treated with an acid, or sometimes an alkali. This method is now never used for accurate work.

(2) The determination of the weight of the substance which will combine with 8 gms. of oxygen.

This may be done either by making a known weight of the element into its oxide, and weighing the oxide, or by starting with a known weight of oxide, reducing it to the element, and weighing the element.

(3) Determination of the weight of silver necessary to precipitate a known weight of the chloride of the element.

Thus, to determine the equivalent of sodium, sodium chloride is taken. A known weight of the salt is dissolved in water, and silver nitrate solution added until precipitation is complete. The precipitated silver chloride is filtered off through a quantitative filter-paper, or a weighed Gooch crucible, washed, dried, ignited (if a paper is used), and weighed. From the weight of the silver chloride the weight of chlorine in the salt is obtained. The equivalent is calculated by finding the weight of metal combining with 35.457 gms. of chlorine.

Alternatively, silver may be taken as the standard, and the weight of silver required to precipitate a known weight of the chloride may be calculated. The equivalent of the compound is that weight of it which is precipitated by 107.880 gms. of silver. The equivalent of the metal is found by subtracting the equivalent of the chlorine present from the equivalent of the chloride.

(4) By displacing another element from combination.

Take, as an example, the determination of the equivalent of copper by adding a known weight of zinc to copper sulphate solution. Copper

This uncertainty about the definition of the element is quite a modern development, dating from the time of the discovery of radioactive disintegration. It was certainly unknown in the eighteenth and nineteenth centuries, and at the time that Dalton lived the idea of an element was quite fixed, as also was that of the atomic nature of matter. Two Irish chemists who preceded Dalton, Bryan Higgins (1737-1820) and William Higgins (1769-1825) got so far as to suggest that chemical combination was due to the union of single ultimate particles of the combining substances, but made the false assumption that the ultimate particles of all substances had the same weight.

There can be no doubt that the time was ripe for the atomic theory; many experimental facts were leading to this inevitable conclusion. It was left to Dalton (1766-1844) to propound the theory—the most far-reaching in its consequences that chemistry has ever known.

9. Dalton's Atomic Theory.—Dalton's views may be summarised in the following terms:—

(1) Elements are made up of atoms, which are indestructible. All atoms of the same element have the same weight, and are similar in size and shape.

(2) Compound atoms are formed by the union of elementary atoms in simple proportions.

Young has pointed out how closely related these statements are to the views of Lucretius. Thus, the first statement of Lucretius when modified to suit the Dalton theory, reads:—

(1) Atoms have different weights, but the number of weights is finite, and there is an infinite number of atoms of each weight.

All that is required is the substitution of the word weight for shape.

(2) Chemical elements consist of one kind of atom only.

(3) Actually the atoms move with a speed very much less than that of light. Dalton did not investigate the speeds of atoms, but the velocities of molecules of gases have since been determined by the aid of the kinetic theory (see § 121, where a table of molecular velocities is given). The most rapidly moving atom moves (at N.T.P.) with a speed no greater than that of a rifle bullet.

There seems to be no doubt that Dalton arrived at his theory on purely physical lines, and that he was very much influenced by Newton. Dalton probably had these ideas in his mind for some years before making them public, and he frequently mentioned the theory, or at least isolated points in it, in his lectures.

The theory explained in a very convincing way the various laws of chemical combination that had already been formulated.

The fact that compounds always contain their constituent elements combined in fixed proportions follows, since combination can only take place between atoms, and these have definite weights.

If two elements, *A* and *B*, combine to form more than one compound,

the molecules of the compounds must be made up of 1 atom of $A + 1$ atom of B , 1 atom of $A + 2$ atoms of B , 1 atom of $A + 3$ atoms of B , 2 atoms of $A + 1$ atom of B , etc. Since the mass of an atom of A is constant, as is also that of an atom of B , the compounds must obey the Law of Multiple Proportions.

When it came to Gay-Lussac's Law of Combining Volumes, however, Dalton's theory experienced difficulties. It was known, for example, that one volume of hydrogen combined with one volume of chlorine to form two volumes of hydrogen chloride. Dalton's theory postulated that combination took place between simply related numbers of atoms, and that in all probability, in this case, it was between single atoms. Berzelius indeed believed, as a result of combining Dalton's theory with Gay-Lussac's Law, that equal volumes of gases under the same conditions of temperature and pressure contained an equal number of atoms. On applying this hypothesis to the data we have before us, we see that it leads to the conclusion that one atom of hydrogen combines with one atom of chlorine to form two "atoms" of hydrogen chloride. The conception of an atom necessitated the possibility of obtaining a single "atom" of hydrogen chloride, and hence this single "atom" would contain half an atom of hydrogen and half an atom of chlorine. This meant that the atoms must be divisible into two halves, and this was in direct contradiction to Dalton's statement that the atom was indivisible, a statement upon which he always laid great emphasis. Instead of looking for the error, however, in the assumption that equal volumes of gases contain the same number of atoms, he made the statement that gases do not combine exactly in simple proportions, and that whenever figures were obtained which agreed with that result, they were due to experimental error—a most remarkable thing to say in face of all the evidence. The correct interpretation of the matter was given by Avogadro, who pointed out the difference between atoms and molecules, and put forward his famous Hypothesis (1811). The latter was, however, disregarded until the middle of the century, and until this time the whole question remained in considerable confusion. When Avogadro's Hypothesis was accepted, the molecules of elementary gases were assumed to be diatomic.

10. Avogadro's Hypothesis.—It must be emphasised that Dalton's view of the atom was that it was the smallest particle of a substance that could exist, irrespective of whether the substance was an element or a compound. It was quite usual for Dalton to talk of an atom of a compound. Avogadro, however, recognised that the smallest particle of a compound could actually be further subdivided into its component atoms, and the term molecule was applied to the smallest particle of a compound that retained the chemical properties of the compound. *The molecular weight of a compound is the sum of the atomic weights of its constituent atoms.*

Avogadro, therefore, stated that "equal volumes of gases, under the same conditions of temperature and pressure, contain the same number of molecules". The same hypothesis was put forward independently by Am^{me} a little later.

At that time it was not possible to prove this hypothesis by direct experiment.

Avogadro's Hypothesis was not generally accepted until some forty-seven years later, when Cannizzaro revived it. Its fall into abeyance was due to the fact that the idea of the distinction between atom and molecule was not fully grasped. The Hypothesis has now become so much a part of our working stock in connection with gases that we do not stop to think whether it is true or not. It has shown that the common elementary gases are at least diatomic, and has provided a means of determining the atomic weights of the gaseous elements, which atomic weights are confirmed by many other methods. It is not, however, strictly true, for as in the Law of Volumes, upon which it depends, there are deviations due to the fact that no gas is ideal. The account which has to be taken of these deviations is fully explained in § 128.

11. Methods of Determining Atomic Weights.—The atomic weight of an element was defined as the ratio of the weight of one atom of the element to that of an atom of hydrogen, though as explained above it is now usual to base atomic weights on the oxygen standard, and the definition then becomes *the ratio of the weight of an atom of the element to one-sixteenth of the weight of an atom of oxygen*.

At one time the atomic weight of an element was regarded as one of its most important constants, and particularly after the advent of the Periodic Law (§ 11, d) the atomic weight was supposed to be the factor determining the properties of an element. It is now known that it is not the atomic weight that is the important thing about an element, but the atomic number. The atomic number is defined as the numerical value of the net nuclear charge of the atom of the element, reckoned in units of positive charge equal in magnitude to the electronic charge (see § 37). This is the number of the element in the series of elements written in the order of the periodic table, taking account of the missing elements (i.e., ascending order of atomic weight with certain departures indicated by the properties of the elements). The atomic weight of an "element" is not necessarily a constant. As stated above ordinary "elements" consist of a mixture of isotopes, i.e., elements with identical chemical properties but different atomic weights (§ 38). It is true that the composition of these isotopic mixtures is always the same when the elements are prepared in the usual way, and the atomic weight will therefore appear to be a constant; but there is the likelihood that the composition of the mixture may alter with the source of the element, and then the atomic weight would differ from that usually determined. In fact,

examples are known where the atomic weight of an element determined from some mineral source depends upon the age of the mineral, the composition of the isotopic mixture of atoms being different.

The atomic weight, then, can no longer be regarded as a fundamental constant of an element, and although much work has been done on the accurate determination of atomic weights, this has to a certain extent been wasted, since atomic weights have not the significance originally assigned to them. On the other hand, such accurate determinations led to the improvement of analytical methods. An accurate knowledge of atomic weights is, moreover, essential in the quantitative analyses on which the results of most chemical investigations depend.

We can only consider here the fundamental principles of atomic weight determinations. Much of the theory of the different processes employed is more fully dealt with in other parts of the book.

1. GASEOUS ELEMENTS.—The atomic weight of a gaseous element (with the exception, of course, of hydrogen) is obtained from the relationship

$$\text{vapour density} = \text{molecular weight} / 2.$$

Common elementary gases are all diatomic; the exceptions are the inert gases. Hence, if the molecular weight is known, the atomic weight is found by dividing by two.

The relationship quoted above depends upon the validity of Avogadro's Hypothesis. Strictly, the Hypothesis only holds for ideal gases, and no gas is perfect. Gases do, however, approach ideality at low pressures, and so, the lower the pressure, the more nearly true is Avogadro's Hypothesis and the above relationship. The correction necessary for ordinary gases is explained in full in § 128. The student is recommended, however, not to take it into account at this point, but to assume that Avogadro's Hypothesis is correct.

The method requires, then, a determination of the density of the gas. The exact determination of the density of a gas can be carried out in three ways:—

(a) *Regnault's Method*.—This consists simply of weighing a known volume of the gas under definite conditions of temperature and pressure. Regnault used large glass globes which were first evacuated, then filled with the gas, the difference in the weights of the globe giving the weight of the gas. The volumes employed were about 50 litres, but in these days of more accurate balances it is found much more convenient to use small globes of about 2 litres capacity, or even less.

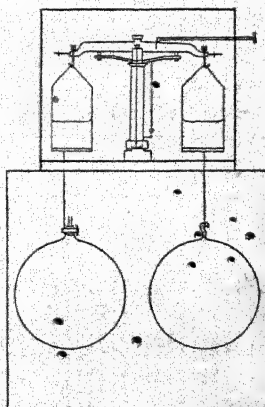


FIG. 2.—Regnault's Apparatus.

The globe, of which the volume must be known, must first of all be very carefully dried. This is done by repeatedly filling the globe with air dried over phosphorus pentoxide, and then with the pure dry gas under investigation. The vessel is then completely evacuated. The purpose of this process is to replace any film of moisture on the inside of the glass globe with a film of the gas under examination. The globe is then hung from the beam of a balance and counterpoised by a similar globe, together with a few weights. This is to compensate for the film of moisture which is always to be found on the outside of the glass globe, and also for changes in pressure and temperature in the neighbourhood. The vessel is then filled with gas at a known pressure, usually near 760 mm., and at a known temperature, usually 0°C . It is then weighed again, the additional weights placed on the side of the counterpoising globe being approximately equal to the weight of the gas.

Corrections now have to be made for buoyancy. The vessel, first evacuated, and then filled with a gas at atmospheric pressure, expands a little. When a vessel is weighed in air, the weight obtained is the actual weight of the vessel *in vacuo* less the weight of air displaced. The vessel when full of gas displaces more air than when it is evacuated, and consequently an addition will have to be made to the weight determined. This will be equal to the difference in volume of the globe, multiplied by the weight of 1 c.c. of air under the laboratory conditions.

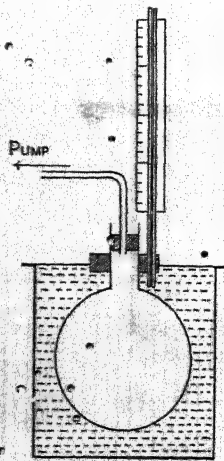


FIG. 3.—
Travers's Apparatus
(diagrammatic.)

Travers devised a method of determining this contraction when the globe was evacuated. The globe was placed inside a closed vessel, with its neck passing through a hole in the stopper (Fig. 3). Also, through another hole in the stopper, passed a calibrated vertical capillary tube. The vessel was completely filled with water, and placed in a thermostat. The globe was then evacuated, and as its volume decreased, the level of the water in the capillary tube fell. From the scale, the volume change could be read off directly.

The actual volume of the globe is determined by filling it with water and weighing. This weight must be corrected for the tempera-

ture of the water, and for the weight of air displaced by the globe.

Knowing the weight and the volume of the gas, the density, in grams per litre, can be calculated. For the purpose of molecular weight determination, the density referred to oxygen as 16 is required, and consequently the density of oxygen in grams per litre must be known, or determined. The molecular weight is then calculated as above. Correc-

tion must be made for the failure of Avogadro's Hypothesis, and the method of applying this is given in § 128.

(b) *The Volumeter Method* (Guye and Pintza).—The principle of the method is the reverse of the last, the volume of a known weight of gas being determined.

The apparatus used by Guye and Pintza in their determination of the density of nitrogen is shown in Fig. 4.

The volume of the globes A and B were determined by finding the weight of water filling them at 0° C. The volume of the "dead space" between the marks *a* and *b* and the tap G, and the zero of the manometer D were also determined, and the space between the taps E, F and G. The tube H contained coconut charcoal, and was first evacuated and weighed and then attached to the apparatus by a ground-joint (not shown in Fig. 4). The apparatus which was perfectly dry, and had been filled with the gas several times, was evacuated, and then filled with the gas slowly, up to about atmospheric pressure. The bulbs were immersed

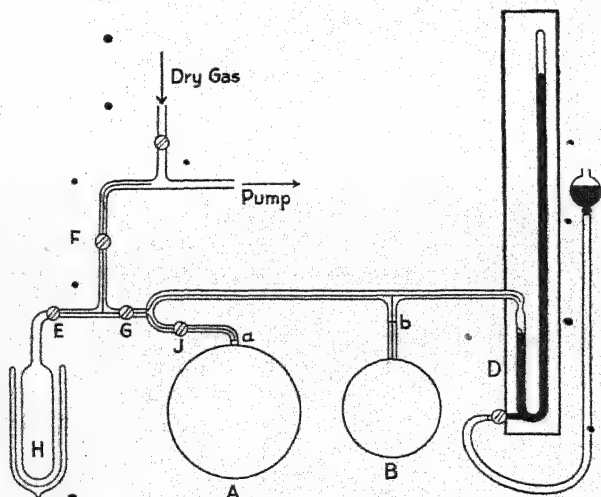


FIG. 4.—Guye and Pintza's Volumeter Method.

in melting ice, and the taps F and G closed, the mercury adjusted to the zero D, and the pressure of the gas read. The space E, F, G, was then evacuated, F closed, and by opening the taps E, G and J, the gas was absorbed by the charcoal in the absorption tube H, the charcoal being cooled in a mixture of solid carbon dioxide and ether. When nearly all the gas had been absorbed, taps E and G were closed, and the pressure of the gas remaining in the apparatus determined. The gas contained in the space E, F, G, was pumped out and measured, and the absorption

tube removed from the apparatus and reweighed. The weight of the gas absorbed by the charcoal was thus found.

From the difference in pressure before and after the experiment, and the amount of gas left in the "dead space", the volume of gas absorbed was calculated. Its weight was known, and hence the density was calculated, corrections being applied for deviations from Boyle's Law.

(c) *The Buoyancy Method.*—A more modern and precise method of measuring gas densities depends upon determining the buoyancy of the gas, and employs a micro-balance. The latter consists of a small quartz bulb, Q (Fig. 5), of about 0.5 c.c. capacity, which is evacuated, and attached to a quartz beam (resting on a knife-edge, K), the motion of which is restricted by two plates, A.A. The whole is enclosed in a glass cage, provided with an entrance tube, fitted with a tap. The apparatus is so adjusted that after evacuation, and filling with the gas under test at a known pressure, the end of the beam, B, is at the zero position of a scale in a telescope through which the beam is viewed. The vessel is

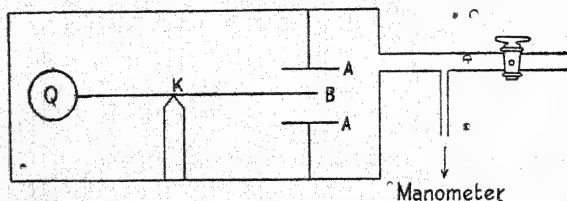


FIG. 5.—Microbalance (very diagrammatic).

again exhausted, and oxygen is then admitted to such a pressure that the beam is again at the zero position. Low pressures are used, so that Boyle's Law may be supposed to hold with accuracy for the two gases. It may readily be shown that if D is the density of the gas, D_1 the density of oxygen, p the pressure of the gas, and p_1 the pressure of oxygen,

$$\frac{D}{D_1} = \frac{p_1}{p},$$

or,
$$D = \frac{p_1 D_1}{p}.$$

The advantages of the method are that it requires only a very small quantity of gas, and the work is quickly carried out. With a micro-balance similar to that described, the density of radium emanation, of which only 0.75 cubic millimetres was available, was determined. Aston used this apparatus in 1914 to determine the densities of samples of neon, in attempting to separate its isotopes.

The buoyancy method has been used by Woodhead and Whytlaw-Gray in the determination of the atomic weights of xenon (1931) and carbon (1933). The balance used in the latter determination was constructed entirely of fused quartz, and was a modification of that

previously described, being of the fibre suspension type. The buoyancy bulb in Fig. 6, had a capacity of 8 c.c., and was counterpoised by a smaller bulb with a hole in it, and a small sphere of silica. The method employed was to determine the ratio of the pressures at which carbon

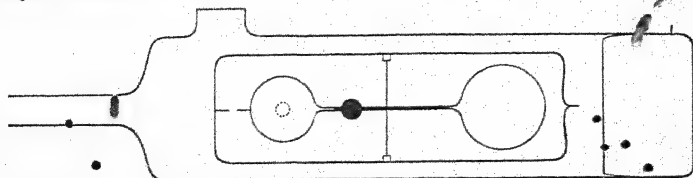


FIG. 6.—Fibre Suspension Buoyancy Balance (Plan).

monoxide and oxygen have the same densities. The balance case was exhausted, and one of the pure gases run in very slowly, through a U-tube cooled in liquid air, until the balance floated. Then a final adjustment of pressure was made until the balance pointer was at the zero mark. The same process was repeated with the other gas. Numerous corrections were necessary, which cannot be described here.

The following table gives some of the results:—

TABLE I.—DENSITY OF CARBON MONOXIDE

Series.	• Approx. pressures (mm).		Uncorrected ratio.	Corrections.	Corrected ratio.
	O ₂ .	CO.			
I. (0° C.)	382.8	437.2	0.87526	—0.00010	0.87516
II. (19.8° C.)	181.9	207.8	0.87535	—0.000123	0.87523
III. (19.8° C.)	361.9	413.5	0.87524	—0.000112	0.87514
IV. (19.8° C.)	572.3	654.0	0.87509	—0.000099	0.87500

To obtain the molecular weight of carbon monoxide the value of the ratio at zero pressure (§ 128) must be obtained. This is done by plotting the ratio against the pressure, and continuing the straight line to cut the axis at zero pressure. In this way, three values for the ratio at zero pressure can be obtained from series II., III. and IV. The value from series I. was not considered to be so accurate as those from the other series.

TABLE II.—MOLECULAR WEIGHT OF CARBON MONOXIDE

	Limiting ratios.	Mol. Wt. of Carbon Monoxide.
From Series II. and III.	0.87533	28.010
" " II. and IV.	0.87534	28.011
" " III. and IV.	0.87537	28.011

The molecular weight of the carbon monoxide was calculated from the ratio by multiplying by the molecular weight of oxygen (32). Taking the value for the molecular weight 28.011, this gives 12.011 for the atomic weight of carbon.

(d) Under certain circumstances the methods described in § 12 for finding the vapour densities of compounds may be applied to elements.

2. LIQUID ELEMENTS.—There are only two liquid elements (mercury and bromine), and the atomic weights of these are best determined by converting them into vapours and treating them as gases, or else by using some of the methods for solids.

3. SOLID ELEMENTS.—The relationship used here is *equivalent* \times *valency* = *atomic weight* (§ 6). It is necessary to determine two things: first the equivalent, and secondly the valency. Since the valency is always an integer, it is clear that the accuracy of an atomic weight determination based on this expression depends upon the degree of accuracy with which the equivalent is determined. As this determination can be carried out with all the accuracy of quantitative chemistry, errors in atomic weights arising from this cause are small.

The more difficult task is to decide the valency of the element. There are several ways of doing this.

(a) *The Vapour Density Method.*—In this method the molecular weight of a compound of the element is determined. This can be carried out most conveniently by Victor Meyer's method of determining vapour density (§ 12). For this purpose a compound must be chosen which will vaporise at as low a temperature as possible, and also is not decomposed on vaporisation. As a rule the chloride is the most suitable compound.

Suppose the element A has a valency n . The formula of its chloride will be ACl_n , and, if a is the atomic weight of the element, the molecular weight, M , of the chloride will be $a + 35.5 n$ (since the atomic weight of chlorine is 35.5, approximately). If e is the equivalent, $a = e \times n$. Hence

$$en + 35.5 n = M$$

$$\text{or } n(35.5 + e) = M.$$

and M are known, so n can be calculated. Of course, vapour density determinations will give only an approximate value for M , so the nearest whole number to the value obtained is taken as the valency. The atomic weight is then obtained by multiplying the accurately determined equivalent by the valency.

(b) *The Specific Heat Method.*—As a result of their researches on the specific heats of a number of metals in 1819, Dulong and Petit were able to make the generalisation that the atomic weight of a metal multiplied by its specific heat is equal to 6.4. The Law only holds for metals, and even then there are several exceptions. It certainly would not be accurate

enough to enable a trustworthy figure for the atomic weight to be found without further and more accurate evidence. Its chief use is to determine the valency of an element, of which the equivalent has been determined with all possible accuracy. The Law is more fully discussed in § 142.

As an example, suppose that the equivalent of a metal has been determined by combining it with chlorine, or by precipitation of silver chloride by the chloride of the metal, the following results being obtained: 1.376 gms. of metal combine with 1.000 gm. of chlorine. Owing to the difficult volatility of the chloride, or for other reasons, it is decided to apply the specific heat method rather than find the vapour density of the chloride. The specific heat is found to be 0.032. From the first observations, the accurate equivalent of the metal is $1.376 \times 35.457 = 48.788$. The rough atomic weight is given by the formula, atomic weight \times specific heat = 6.4. This gives for the rough atomic weight, $6.4/0.032 = 200$. It is clear that the only value for the valency which will bring the atomic weight anywhere near this figure is 4, and so the accurate atomic weight is $4 \times 48.788 = 195.152$.

(c) *Use of the Law of Isomorphism.*—The Law of Isomorphism, which is dealt with more fully in § 154, states that *compounds which have similar chemical formulæ have identity of crystalline form* (i.e., they are isomorphous compounds, which will form mixed crystals).

Thus the three oxides, ferric, aluminium and chromium (Cr_2O_3), are isomorphous; they occur in the same crystalline form, and can sometimes replace each other in minerals. The formula of aluminium chloride is easily found from the vapour density, since this substance is readily volatile, and Victor Meyer's method can be applied. The formula obtained is AlCl_3 , when determined at high temperatures, and the formula of the oxide must be Al_2O_3 . Since the other oxides are isomorphous with alumina, their formulæ must be Fe_2O_3 and Cr_2O_3 , and from the percentage compositions of these oxides as determined by analysis, the atomic weights of iron and chromium can be found.

Isomorphism has proved most useful in correcting atomic weights. Thus, before 1836, silver was supposed to have the atomic weight 216, whilst that of copper was taken to be 63.5. Dumas, in studying the sulphide minerals of copper and silver, found that the minerals chalcocite, Cu_2S , and acanthite, silver sulphide, then written AgS , were isomorphous. For various reasons the figure 63.5 was regarded as correct for copper, and hence the formula of silver sulphide was Ag_2S , and the atomic weight of silver 108.

One of the best examples was the application of isomorphism to the determination of the atomic weight of vanadium by Roscoe in 1868. Berzelius assumed in 1831 that the oxide of vanadium was VO_2 , and the atomic weight on that basis was 61. This view was held for almost

forty years. Rammelsberg in 1856 pointed out that the following minerals were isomorphous:—

Apatite,	$3\text{Ca}_3(\text{PO}_4)_2 + \text{CaF}_2 = \text{Ca}_5\text{P}_3\text{O}_{12}\text{F}$.
Pyromorphite,	$3\text{Pb}_3(\text{PO}_4)_2 + \text{PbCl}_2 = \text{Pb}_5\text{P}_3\text{O}_{12}\text{Cl}$.
Mimetite,	$3\text{Pb}_3(\text{AsO}_4)_2 + \text{PbCl}_2 = \text{Pb}_5\text{As}_3\text{O}_{12}\text{Cl}$.
Vanadinite,	$3\text{Pb}_3\text{V}_2\text{O}_8 + \text{PbCl}_2 = \text{Pb}_5\text{V}_3\text{O}_{12}\text{Cl}$.

The formula of the last compound is that based on the Berzelius figure for the valency of vanadium. It is clear that while the first three minerals have analogous formulæ, the last is quite different. Yet all these compounds are isomorphous, and hence their formulæ should be similar, and the valency of vanadium should be 5.

Roscoe showed that Berzelius had actually mistaken an oxide VO for the element itself.¹ The formula which had been written $\text{Pb}_5\text{V}_3\text{O}_{12}\text{Cl}$, should therefore have been $\text{Pb}_5(\text{VO})_3\text{O}_8\text{Cl}$ or $\text{Pb}_5\text{V}_3\text{O}_{12}\text{Cl}$. Working with pure compounds he obtained the atomic weight, 51.4.

Beryllium behaves in many ways like aluminium, and was at first assigned a valency of three, and an atomic weight of 14.1. But Mendeléeff found that it should appear in Group II. in the Periodic Table, and should therefore have a valency of two. The atomic weight would then be 9.4. This alteration was made by Mendeléeff, and was later confirmed by the determination of the specific heat of the element at high temperatures, by the discovery by Mallard that the oxide, beryllia, is isomorphous with zinc oxide, and must therefore have the formula BeO , and by the determination of the vapour density of beryllium chloride.

The atomic weight of *zirconium* was believed to be about 67 for some time. Berzelius first assigned the formula ZrO_3 to the oxide, but later altered it to Zr_2O_3 . Gmelin, however, gave the oxide the formula ZrO . The vapour density of the chloride was determined by Deville and Troost by Dumas' method, and found to be 8.16 (air = 1). The molecular weight of the chloride must therefore be $8.16 \times 28.8 = 236$, approximately, since the density of air ($\text{O} = 16$) is 14.4. There must be at least four chlorine atoms in the molecule, since the vapour density is too great for ZrCl_3 . It is too small for ZrCl_5 , so the compound was probably ZrCl_4 . The atomic weight was thus four times the equivalent, 22.3, i.e., 89.2. This was later verified by specific heat observations, and by the fact that the compounds K_2SiF_6 , K_2SnF_6 , and K_2ZrF_6 were isomorphous. The valency of zirconium must therefore be the same as that of tin and silicon, viz., 4.

¹ It may be thought that if this were so, Berzelius' oxide VO_2 would be really $\text{VO}(\text{O})$, i.e., VO_2 , which disagrees with the valency of 5 mentioned; but in Berzelius' time, oxygen was assigned an atomic weight of 8, and water was written HO ; consequently, Berzelius' VO_2 would correspond to V_2O_3 on our system, which would be $(\text{VO})_2\text{O}_3$, i.e., V_2O_5 , when the Berzelius error was rectified.

The atomic weight of *selenium* was derived from the fact that potassium sulphate, K_2SO_4 , and potassium selenate, of which the formula must therefore be K_2SeO_4 , were isomorphous. The amount of selenium in a given weight of the selenate was determined, and hence the atomic weight was found.

(d) *The Periodic Table*.—The Periodic Table is a method of classifying the elements which has numerous advantages. Many systems of classification of the elements have been proposed, but most have proved unsatisfactory. The Periodic Table is by far the most satisfactory classification.

In 1829, Döbereiner showed that if certain sets of three related elements, which he called triads, were considered, the atomic weight of the central element was the mean of the atomic weights of the extreme elements. Thus, the atomic weight of bromine (according to modern standards) is 79.916; the atomic weights of chlorine and of iodine are 35.457, and 126.92, respectively. The mean of the last two is 81.188, which is not greatly different from the figure for bromine. The Law, which is called the Law of Triads, may also be tested with lithium, sodium, and potassium; calcium, strontium, and barium; sulphur, selenium and tellurium, and others.

Döbereiner noted also another type of triad in which the elements were closely related, but possessed atomic weights very close to each other. Thus, iron, nickel and cobalt, form a related series, but their atomic weights are 55.84, 58.69, and 58.94, respectively.

In 1863, Newlands found that when he arranged the elements in order of ascending atomic weight, commencing with hydrogen, every eighth element commenced a new series, the properties of the elements at the same places in the various series being similar. Thus:—

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe

This relationship he called the *Law of Octaves*. It was found, however, that it was not true for the elements of higher atomic weight. It can be seen that even in the three series given above there are certain anomalies, iron, for example, being classified with oxygen and sulphur.

The law found little application, but in 1869 Mendeléeff,¹ quite independently of Newlands, put forward a law which was really an extension of the Law of Octaves. This Law, known as the *Periodic Law*, may be stated as follows:—

The properties of the elements are periodic functions of the atomic weights.

¹ In a paper giving an historical survey of the Periodic System, G. Eisen (Chem. Weekblad, 1930, 27, 378) states that a system approximating to that later proposed by Mendeléeff was put forward by one Cooke, as early as 1854.

PERIOD	SERIES	GROUP																				
		I		II		III		IV		V		VI		VII		VIII		IX		X		XI
		N	N	T	N	T	N	T	N	T	N	T	N	T	N	T	N	T	N	T	N	T
					<i>Lan- thanides</i> 58 — 71 <i>Ce — Lu</i>		72 Hf 178.6		73 Ta 180.88		74 W 183.92		75 Re 186.31		76 Os 190.2		77 Ir 193.1		78 Pt 195.23		79 Au 197.2	
							81 Tl 204.39		82 Pb 207.21		83 Bi 209.00		84 Po		85 At		86 Rn 222					
														</								

RARE EARTH SERIES

First Rare Earth Series:

Lanthanides

58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 II	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2
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Second Rare Earth Series:

Actinides

66 Dy 162.46	67 Ho 164.94	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99	92 U 238.07	93 Np 237	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247
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Mendeléeff arranged the elements in series to show this periodic recurrence in properties. Hydrogen had no analogue amongst the other elements, and was therefore placed in a group by itself. Then followed the first and second series, each comprising seven elements (since the discovery of the inert gases, there are now eight elements in these series). Mendeléeff then found it necessary to have a long series, which consisted of two short series joined together by the chain of "transition elements" (e.g., Fe, Ni and Co), making together 18 elements. This was followed by a similar long series, and this again by a series of 32 elements. The remaining series required to finish the table is incomplete. A copy of the Table¹ is given on the preceding two pages. This has been drawn up to include all the elements at present known, and therefore differs considerably from that proposed by Mendeléeff.

It is not our purpose to enter into a lengthy discussion of the Periodic Table, as this is part of Inorganic Chemistry.² For our present work, it is sufficient to notice that in the vertical columns are found elements that are more or less closely related, and that in any horizontal series the valency with respect to hydrogen increases from 1 to 4 (in Group IV.) and then decreases to 1 again. With respect to oxygen, the valency may increase all the way along the horizontal series from 1 to 7. In these statements, the elements in Group VIII. are omitted, and it should be noted that there are some exceptions.

When Mendeléeff constructed the Periodic Table he found it necessary to put some elements in different groups from those into which they would have fallen according to the values of their atomic weights, in order to place them with elements with which their properties were most in accord. Thus, the element *indium* had always been supposed to be bivalent, and to have an atomic weight 75.8. Its bivalency would bring it into Group II. with zinc, but this place is already occupied by strontium, and there is also no room for it between arsenic (75) and selenium (79). The atomic weight was therefore considered to be wrong, and on determination of the specific heat of the element, its atomic weight was found to be 114.5, confirming Mendeléeff's view that it should be placed in Group III.

As stated above, the atomic weight of beryllium was also corrected by this method.

(c) *The Physical Method.*—In this method, the relative amounts and respective atomic weights of the different isotopes present in an element are determined. Within recent years it has become possible to determine atomic weights in this way to a degree of accuracy equivalent to that obtainable by ordinary gravimetric analysis. It has the additional advantage that only a very small amount of the element is

¹ This Table is based on one proposed by T. S. Wheeler (*Chemistry and Industry* 1947, p. 639).

² For a more complete account, the student is advised to see Sharwood Taylor's "Inorganic and Theoretical Chemistry".

required for a determination, and the substance used need not be pure. The method is described in detail later (§ 41).

12. Methods of Determining Vapour Densities.—In § 11 the determination of vapour density has been referred to as being important in finding atomic weights. It is also a very valuable method of finding the approximate molecular weight of a substance in the gaseous state.

The vapour density is the ratio of the masses of equal volumes of the vapour and of oxygen, the latter being taken as 16 under the same conditions of temperature and pressure.

(a) *Victor Meyer's Method.*—There are several methods of determining vapour density, of which the most frequently used is that due to Victor Meyer. In this, the volume occupied by a known weight of vapour is determined.

One form of the apparatus is shown in the accompanying figure (Fig. 7). A long tube usually made of glass, but sometimes, when higher temperatures are necessary, of porcelain, platinum, or quartz, has a bulb at one end. This tube is the one in which the substance is vaporised. It is surrounded by a jacketing tube made of suitable material. A copper tube, even for comparatively low temperatures, is much more useful than a glass one, although the latter is more commonly used. The outer jacket contains some liquid boiling at a considerably higher temperature than the substance to be placed in the inner tube. Where a liquid is used, of which it is not desirable to allow the vapour to escape into the air, a condenser may be fitted. A side tube is attached to the inner tube, bent as shown, and passed under water or mercury in a trough. A graduated tube is filled with the liquid in the trough, and inverted in it, over the end of the side tube. The substance is introduced into the vaporising tube in a small bottle of the shape shown. First, the inner tube is dried thoroughly, and a little asbestos pad placed at the bottom to break the fall of the bottle when it is put in. A liquid is placed in the outer jacket and heated to boiling until no air bubbles appear in the trough. While this is going on, the small tube is weighed, filled with the substance under investigation, and weighed again. The difference gives the weight of substance taken. The stopper of the vaporising tube is now removed, the graduated tube placed in position over the end of the delivery tube, the small bottle dropped in, and the vaporising

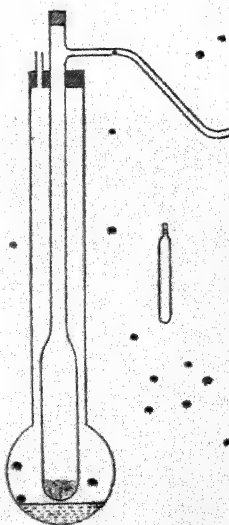


FIG. 7. — Apparatus for Victor Meyer's Method of determining Vapour Densities.

tube re-closed. The stopper is immediately blown out by the pressure of the vapour and bubbles of air are collected in the graduated tube. The total volume of air pushed over is the volume of air displaced by the vapour, and is therefore the volume of the vapour. The temperature of the room and the atmospheric pressure are taken, and the volume is also corrected for vapour pressure of water if the air displaced is collected over water. The density of the vapour in grams per c.c. is calculated, and also the density referred to oxygen as 16, from which the molecular weight can be obtained.

The following is the calculation involved: Let the weight of substance used be W grams, and the volume of vapour, v c.c. Let the temperature of the room be $t^\circ \text{C.}$, and atmospheric pressure P mm. If the pressure of water vapour at this temperature is p mm., the actual pressure of the air collected is $P - p$ mm.

The corrected volume of air is V c.c., given by

$$V = \frac{273 (P - p) v}{760 (t + 273)}$$

The density of the vapour in grams per c.c. is $\frac{W}{V}$.

The molecular weight of the vapour is $22,414 \times \frac{W}{V}$.

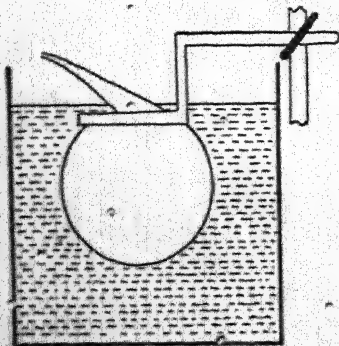


FIG. 8. — Dumas' Apparatus for determining Vapour Density.

(b) *Dumas' Method.* — This method consists in finding the weight of a known volume of vapour.

A large bulb of the shape shown in Fig. 8 is taken, and weighed full of air. It is then slightly warmed with its mouth under a little of the liquid in a dish. On cooling a few c.c. of the liquid will be sucked into the apparatus. The bulb is then placed in a heating bath, and is conveniently held down by an iron ring, as shown in Fig. 8. The liquid in the heating

bath is boiled, and when the last drop of liquid in the bulb disappears, the bulb is sealed off, care being taken to preserve any glass which may have been removed from the end. It is possible to seal the bulb without removing any glass. The bulb is now filled with the vapour of the liquid, and is reweighed, when cool. To find the volume of the

bulb, the end is broken off under water, when the water rushes in, as the vapour will now be under considerably reduced pressure. On reweighing the bulb the weight of water which it contains can readily be found, and hence its volume. The temperature and pressure have to be taken (i.) when the bulb is full of air, and (ii.) when the bulb is filled with vapour and is about to be sealed off.

Calculation.

Weight of bulb full of air	= W gms.
Weight of bulb full of vapour	= w gms.
Weight of bulb full of water	= W_1 gms.
Temperature at commencement	= $t^\circ \text{C.}$
Pressure at commencement	= p mm.
Temperature just before sealing off	= $T^\circ \text{C.}$
Pressure just before sealing off	= P mm.
Volume of air filling bulb at $t^\circ \text{C.}$ and p mm.	= $W_1 - W$ c.c.

$$\text{Corrected volume} = \frac{273 p (W_1 - W)}{760 (t + 273)} \text{ c.c.} = V \text{ c.c.}$$

The weight of this volume of air =
0.00129 V gms.

Hence true weight of vapour filling bulb = $w - W + 0.00129 V$ gms. But this filled the bulb at $T^\circ \text{C.}$ and P mm., and the volume of the vapour corrected to N.T.P. will be

$$\frac{273 P (W_1 - W)}{760 (T + 273)} \text{ c.c.} = V_1 \text{ c.c.}$$

Hence density of the vapour at N.T.P.
= $(w - W + 0.00129 V) / V_1$ gms./c.c.
The error should not exceed 2 per cent.

A more modern form of the apparatus is shown in Fig. 9. This works on essentially the same principle, and the results are calculated in the same way. The wide outer vessel contains a liquid of higher boiling point than that of which the vapour density is required.

The vapour of this liquid heats the bulb, and is condensed by a condenser attached at A. The temperature is read by a thermometer passing through the lid of the vessel. This is a convenient form for carrying out determinations at the higher temperatures.

(c) *Hofmann's Method.*—The principle of the method is to introduce

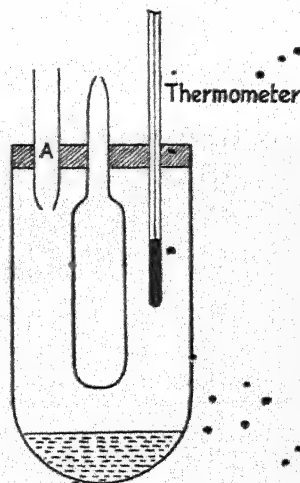


FIG. 9.—Modified Form of Dumas' Apparatus.

a known weight of the liquid into the vacuum at the top of a barometer surrounded by a heating jacket. The liquid evaporates and its volume is measured by the depression of the mercury.

The arrangement of the apparatus is shown in the accompanying diagram (Fig. 10). A small tube (that used for the Victor Meyer determination may be used here) is weighed empty, and then filled with liquid. It is sometimes possible to pour the liquid into these bottles, but if this is not possible, the filling is easily accomplished by warming a little with the mouth of the bottle under some of the liquid in a dish. On cooling, the liquid is forced in. A piece of glass tube drawn out to a capillary may also be used as a pipette. The bottle is then introduced into the graduated barometer tube, the height of the mercury having been noted. When all the liquid has evaporated, the mercury will reach a constant level, the height of which is again read. The difference between the two gives the pressure to which the vapour is subjected, and the volume of the vapour will be the total volume of the space above the mercury. The temperature will be that of the heating jacket. The corrected volume of vapour is found; its weight is known, and hence the density can be found.

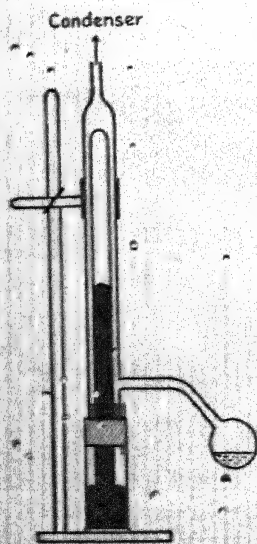


FIG. 10. — Hofmann's Apparatus for determining Vapour Density.

Calculation.

Weight of bottle, empty = W gms.

Weight of bottle filled with liquid = w gms.

Hence, weight of liquid taken = $w - W$ gms.

Volume occupied by vapour = V c.c.

Pressure = $H - h$ mm., where H is the initial, and h the final height of the mercury in the tube.

Temperature = $T^{\circ}\text{C}$.

Hence, corrected volume of vapour = $\frac{273 (H - h) V}{760 (T + 273)} \text{ c.c.} = V_1 \text{ c.c.}$

Weight of this volume = $w - W$ gms.

Hence, density = $(w - W)/V_1$ gms./c.c.

The molecular weight of the vapour will be given by $22,414 \times D$, where D is the density in gms./c.c.

This method is capable of giving quite accurate results, but the apparatus is cumbersome, and difficult to arrange and read. It also

suffers from the disadvantage that, in its ordinary form at any rate, it cannot be used for determining vapour densities at high temperatures.

In another method of determining vapour density, making use of the glass-spring tensimeter, the pressure exerted when a known weight of substance is vaporised at a known temperature is determined. The apparatus is shown in Fig. 11. The vaporisation bulb, A, is made of glass, or preferably of quartz, and has a flattened spiral tube, B, attached, which is connected to a quartz thread, C. The spiral tube and thread are surrounded by a glass vessel, which can be exhausted, and is supplied with a manometer. The volume of the bulb, A, is determined in a separate experiment, and a known weight of substance is placed in it. The bulb is then exhausted and sealed. On heating in a thermostat or furnace, the substance vaporises, and exerts a pressure which tends to open out the spiral glass spring, and causes a movement of the quartz thread, which can be observed through a telescope, or by means of a mirror, M, attached to the end of the thread. By admitting air to the vessel surrounding the thread and spring, the pressure inside and outside the spring may be made the same, when the pointer will return to its zero position. The pressure of air admitted is measured by means of the manometer, and gives the pressure inside the bulb. The temperature to which the bulb is heated must be determined accurately, and this is best done by means of a platinum resistance thermometer, or a thermo-couple. The mass of vapour is known, and also the pressure it exerts when confined in a known space, so that the vapour density is readily calculated.

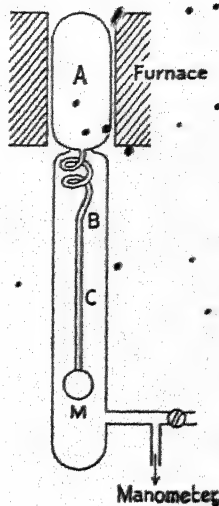


Fig. 11.—Glass-Spring Tensimeter.

13. Some Classical Experiments on Combining Weights and Volumes.

1. COMPOSITION OF WATER BY WEIGHT.—(a) *Dumas' Method*.—The rather difficult work of finding the ratio in which hydrogen and oxygen combine by weight was first taken up by Dumas in 1842. A diagram of the apparatus is given in Fig. 12.

Hydrogen was made by the action of dilute sulphuric acid on zinc. The gas was impure, and an elaborate system of purification had to be devised. The gas was passed through a series of seven U-tubes containing (1) lead nitrate, to remove hydrogen sulphide; (2) silver sulphate, to remove arsine, stibine, etc.; (3) three tubes containing caustic potash, to remove acid vapours; and (4) a tube of concentrated sulphuric acid cooled in ice, and a tube containing phosphorus pentoxide to dry the gas.

The purified gas was passed over carefully dried copper oxide con-

tained in a hard glass bulb tube. This tube was first disconnected from the apparatus, exhausted and weighed. After replacing the bulb tube, all air was swept out of the apparatus by hydrogen, and the stream of hydrogen continued for ten to twelve hours, during which the copper oxide was heated by means of a spirit lamp. The hydrogen reduced the copper oxide to copper, and water was formed which was collected in a small bulb tube, followed by four drying tubes containing concentrated sulphuric acid on pumice, or phosphorus pentoxide, the object being to prevent the loss of any water vapour which might not have been condensed in the bulb. The bulb and drying tubes which had been

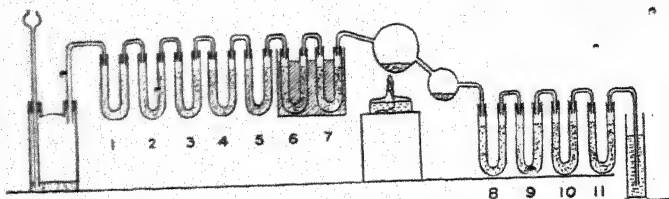


FIG. 12.—Dumas' Apparatus for determining the Composition of Water by Weight.

weighed before the experiment were reweighed at the end, the difference giving the weight of water produced. The copper produced was allowed to cool in a stream of hydrogen, and the bulb was then disconnected, exhausted and weighed. The difference in weight of this tube before and after the experiment gave the weight of oxygen removed, and which was now in the water. By subtracting this weight of oxygen from the weight of water produced, the weight of hydrogen in the water was obtained.

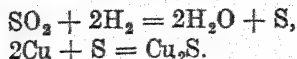
The result obtained, as a mean of nineteen experiments, was:—

	Per cent. by weight.	Combining ratio.
Hydrogen	11.136	1.00
Oxygen	88.864	7.98

There are several sources of error in this experiment:—

- (1) A small quantity of air, dissolved in the sulphuric acid used, passed on with the hydrogen, and the oxygen present consequently combined with some of the hydrogen in the hot copper oxide tube.
- (2) The copper, on cooling in hydrogen, absorbed some of the gas.
- (3) The drying of the gas with concentrated sulphuric acid produced some sulphur dioxide, which on passing over the heated copper oxide

with hydrogen lost its oxygen, water being formed, the sulphur remaining combining with the copper to form cuprous sulphide.



Various improvements have been made in this method. Keiser used hydrogen adsorbed in palladium. The gas was pumped over heated copper oxide, the water formed being weighed. The weight of hydrogen used was obtained by weighing the palladium before and after the experiment, and thus it was not necessary to weigh the copper oxide.

(b) *Morley's Method.*—The classical experiment of Morley for the determination of the composition of water by weight is now taken as providing the most accurate ratio. Indeed, it has been said that this is the most accurate chemical research ever carried out.

The gases, hydrogen and oxygen, were very carefully purified and weighed in glass globes. A tube was constructed of the form shown in Fig. 13, which has two drying tubes, *aa*, and two platinum jets, *pp*. The tube was exhausted and weighed. The gases were then passed into the apparatus, one down one side, and one down the other, and they were ignited at the platinum jets by passing sparks between the electrodes, *ee*. During the combustion, the tube was immersed in cold water, and at the end of the experiment it was placed in a freezing mixture to freeze the water produced. The excess gas was then pumped out of the apparatus, being dried on its way by the drying tubes, *aa*, and was analysed. The total weight of hydrogen and oxygen used was found to agree with the weight of water formed.

The mean result of twelve experiments was:—

$$\begin{aligned} \text{hydrogen: oxygen} &= 1 : 7.9396 \\ &= 1.0076 : 8.0000 \end{aligned}$$

(c) *Noyes' Method.*—This method, which also gives very accurate results, was developed by Noyes in 1903. The apparatus is shown in Fig. 14. Pure hydrogen was prepared by the electrolysis of barium hydroxide solution in an apparatus somewhat similar to that used by Burt and Edgar some time later in determining the volumetric composition of water (Fig. 15). The gas was passed into a tube containing palladium, the tube having previously been exhausted. Pure oxygen, also made by the electrolysis of baryta, was now pumped in, whilst the tube containing the palladium-hydrogen was heated. Combination of

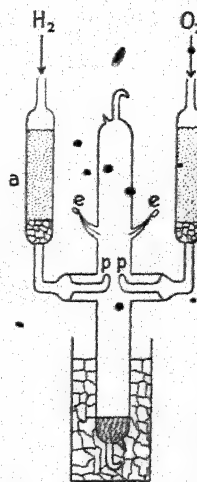


FIG. 13.—Morley's Combustion Tube.

the hydrogen and oxygen took place, with the formation of water, which was collected in a cooled tube, weighed before and after the reaction. The gases left in the tube were pumped off and weighed. The weight of hydrogen in the water was given directly by the difference in

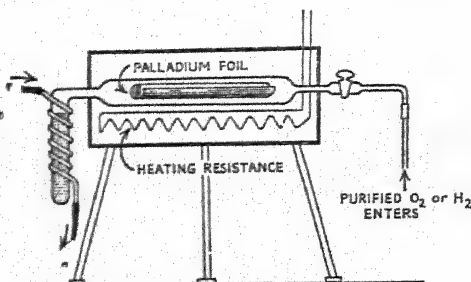


FIG. 14.—Noyes' Apparatus.

weight of the palladium before and after the experiment, whilst the weight of oxygen was obtained by finding the weight of water, and subtracting the weight of hydrogen from it. As a mean of several experiments, the ratio of the weights of hydrogen to oxygen in water was found to be 1.0078 : 8.

2. THE COMPOSITION OF WATER BY VOLUME.—This was a somewhat easier problem than the determination of the gravimetric composition, and consequently we find it was investigated much earlier than the latter. In 1781, Cavendish made a determination using the explosion method, and obtained, as a result, the ratio hydrogen : oxygen = 202 : 100. In 1801, Nicholson and Carlisle discovered that water could be decomposed by passing an electric current through it, and Cruickshank collected the gases and found the ratio of their volumes.

Gay-Lussac and Humboldt, in the course of their experiments on the combining volumes of gases which ultimately led to the Law of Gaseous Volumes, found the ratio hydrogen : oxygen to be 199.89 : 100, and Bunsen found 200 : 100.

The most accurate of the experiments made on the determination of this combining ratio during the last century were those of Alexander Scott, between 1887 and 1893. The hydrogen was obtained by passing steam over sodium, and the oxygen by heating silver oxide. The purified gases were exploded, and the ratio found was hydrogen : oxygen = 200.285 : 100.

By converting the weights in Morley's experiment to volumes by means of the known densities of the gases, the ratio obtained was 200.269 : 100.

The most accurate research carried out for the determination of the volumetric composition of water was that of Burt and Edgar (1915).

The gases were obtained in a specially pure state by the electrolysis of barium hydroxide solution in the apparatus shown in Fig. 15.

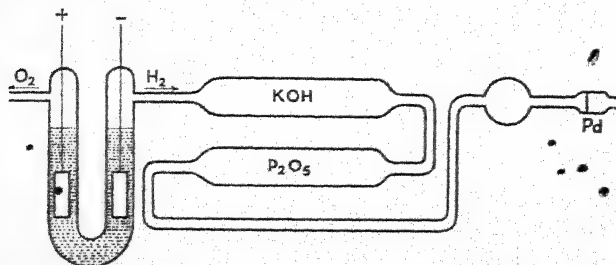


FIG. 15.—Burt and Edgar's Apparatus for the Preparation of Pure Hydrogen.

The hydrogen was dried by passing over caustic potash and phosphorus pentoxid, and then further purified by one of two methods: either by passing the gas over coconut charcoal cooled in liquid air, which absorbs oxygen and nitrogen, but hydrogen hardly at all, or by passing through a tube containing palladium black, which causes the combination of any oxygen present with hydrogen, to form water catalytically. The gas was then passed through a palladium membrane heated electrically. This is permeable to hydrogen, but not to any other gas.

The oxygen was prepared in the same apparatus, being passed out from the anode side of the U-tube, liquefied and fractionated. Another method was sometimes used to obtain the oxygen, viz., the action of heat on pure potassium permanganate, washing the gas with strong caustic potash solution, baryta solution, and again with potash. It was then dried, liquefied and fractionated.

The gases, obtained in this way in a state of high purity, were passed into a special explosion apparatus, for details of which the original paper must be consulted. The special advantage of the apparatus was the fact that the actual determinations were carried out at 0°C ., and under a pressure of 1 atmosphere, thus avoiding temperature and pressure corrections. As a mean of fifty-nine experiments, the ratio found was hydrogen : oxygen = 2.00288 : 1 at N.T.P.

It is interesting to note that the variations in the results obtained by these methods may be explained, at least partially, by the existence of a heavy isotope of hydrogen, ^2H , and of heavy water. Some doubt is thrown upon the accuracy of all the experiments described owing to a lack of knowledge of how far the heavy isotope was separated from the hydrogen used.

In ordinary hydrogen, the ratio of the masses of the light ^1H , to the heavy ^2H , has been given by Rutherford as 6,500/1. Thus 6,501 mg. of

the mixture will react with the same weight of oxygen as 6,500 mg. of the $^1\text{H}_2$ gas, which makes a difference of nearly 0.0002 in the equivalent. The results of Morley and Noyes are 1.0076 and 1.0078 respectively, showing a degree of uncertainty not far from the 0.0002 mentioned. Presumably the preparation of hydrogen by electrolysis, or by the action of acid on zinc, lowers the proportion of $^2\text{H}_2$ or $^1\text{H}^2\text{H}$ in the gas, for heavy water is obtained from the residues of electrolysis experiments. The effect of adsorption in palladium on the relative proportions of the isotopes may also play some part.

3. THE WORK OF T. W. RICHARDS.—Some of the most accurate determinations of atomic weights by chemical methods were carried out by T. W. Richards at the beginning of the century. He was awarded the Nobel Prize in Chemistry in 1914 for his work in this field. He and his co-workers at Harvard determined the atomic weights of almost all the then known elements, but their work on the atomic weights of silver, chlorine, and nitrogen is probably the most fundamental.

Richards attained great accuracy because of his attention to detail. He took the greatest pains to ensure the purity of the chemicals he worked with, going to extreme lengths to remove all possible errors. In the determination of the atomic weights of the above elements the ratios $\text{Ag} : \text{AgCl}$, $\text{AgCl} : \text{NH}_4\text{Cl}$, and $\text{Ag} : \text{AgNO}_3$ were found. For the first, pure silver nitrate was obtained by recrystallising the substance fifteen times from water, and the substance thus obtained was reduced to silver by fusion on pure lime in an atmosphere of hydrogen. The silver was dissolved in the purest nitric acid and silver chloride was precipitated by the addition of an aqueous solution of sodium chloride which had itself been carefully purified. The silver chloride was filtered through a Gooch crucible, washed, and dried. Although silver chloride is one of the least soluble of substances the amount of it dissolved in the washing water was determined by a nephelometric method, the silver chloride being precipitated by the addition of more silver nitrate and the turbidity compared with that produced with standard solutions. The dried silver chloride was weighed and the ratio of $\text{AgCl} : \text{Ag}$ was found to be 1 : 1.32867.

To obtain the second ratio, pure ammonium chloride was prepared by two distinct methods. In the first, ammonium sulphate was purified from organic matter by treatment with concentrated sulphuric acid and a little potassium permanganate. It was heated with pure lime and the ammonia evolved was passed into pure hydrochloric acid. The solution was evaporated and the product sublimed. To avoid possible reaction of the substance with glass at the temperature of sublimation, quartz vessels were employed. Electric heating was used to avoid any possible contamination by gases from burners. The sublimation was carried out in a closed vessel in an atmosphere of ammonia, and by an

ingenious arrangement the sublimate was collected directly in a weighing bottle which was stoppered inside the apparatus so that at no stage did the ammonium chloride come into contact with the air. The weighed ammonium chloride was dissolved in water and silver chloride was precipitated by addition of pure silver nitrate solution obtained from silver as mentioned above.

In the second method the ammonium chloride was prepared from ammonia obtained by reduction of nitric acid. The ratio $\text{NH}_4\text{Cl} : \text{AgCl}$ was found to be 0.373217 : 1.

For the third ratio very pure silver was dissolved in dilute nitric acid in a quartz flask, and the solution was evaporated to dryness in a slow stream of air. The ratio $\text{Ag} : \text{AgNO}_3$ was found to be 1 : 1.57479.

It is possible using these data and the atomic weight of hydrogen determined by Morley to obtain by a simple calculation the atomic weights of nitrogen, chlorine and silver. The values obtained by Richards were: N 14.0085; Cl 35.4574; Ag 107.881.

SUGGESTIONS FOR FURTHER READING

- "Foundations of the Atomic Theory" (Dalton, Wollaston, T. Thomson, 1802-8). *Alcmbic Club*, No. 2.
"Foundations of the Molecular Theory" (Dalton, Gay-Lussac, Avogadro, 1808-11). *Alcmbic Club*, No. 4.
"A Course of Chemical Philosophy" (Cannizzaro, 1858). *Alcmbic Club*, No. 18.
YOUNG, S. "Stoichiometry." (Longmans, Green, 1918.)
CAVEN, R. M. "The Foundations of Chemical Theory." (Blackie, 1920.)
Richards Memorial Lecture. (*Journal of the Chemical Society*, 1930.)

CHAPTER II

ATOMIC STRUCTURE—PART I

14. The Conduction of Electricity through Liquids.—The discovery of the Voltaic pile in 1800 marked the opening of a new epoch in the history of physics and chemistry. The working of the cell itself was a matter of great interest, and involving as it did the passage of a current through a liquid, research was very soon centred on this aspect of the subject. Indeed, in the year 1801, Nicholson and Carlisle, as mentioned in the previous chapter (§ 13), decomposed water by passing the electric current through it.

The chief investigator in this branch of science, at the time was Sir Humphry Davy, who prepared the alkali metals, sodium and potassium, by electrolysis of their moist hydroxides, i.e., strong solutions of the hydroxides. This work was done in the years 1807–8. During this time, Berzelius and Hisinger, in Sweden (1803–7), had been studying the effect of passing the current through solutions of neutral salts, using various electrodes, and noting the products. In this way, during the first decade of the nineteenth century, a large amount of qualitative data was obtained. So far no quantitative explanations had been given. It was Faraday who first established the quantitative relationship between electricity and atomic weight in his two Laws of Electrolysis, put forward in 1834. These Laws state:—

(1) *For equal quantities of electricity, the amount of decomposition is constant, or the amount of decomposition caused in electrolysis is proportional to the quantity of current passed* (quantity of current is the current multiplied by the time for which it is passed, and is measured in coulombs, or ampère-seconds).

(2) *For the same quantities of electricity passed through different solutions, the amount of decomposition is proportional to the equivalent of the element, or group deposited.* Thus, if the same current is passed successively through solutions of copper sulphate, silver nitrate, and lead nitrate, as can easily be done by connecting the three cells in series, the amounts of the metals, copper, silver and lead deposited, will be in the ratio 31.785 : 107.88 : 103.61.

Sidgwick has pointed out that these laws of electrolysis correspond exactly to the laws of constant and multiple proportions. We now believe that the current is carried through the solution by means of ions, which are charged atoms or groups. The above laws may be rewritten in more modern language: (1) the amount of electricity

associated with an ion is constant; and (2) if an atom can form more than one type of ion (e.g., ferrous and ferric, cuprous and cupric) then the amounts of electricity combined with the same atom bear a simple ratio to one another.

It follows from the first law that for any electrolyte

$$W = Iz, t,$$

where W is the weight of substance liberated, I is the current, and t the time for which the current flows. z is a constant, called the *electrochemical equivalent*. It is characteristic of each element or group.

From the second law it follows that one equivalent of any substance will be liberated by a certain quantity of electricity. This has been determined experimentally to be 96,500 coulombs (± 0.01 per cent.), and is given the name of "the Faraday". It was found with great accuracy by Washburn and Bates in 1912, using the iodine coulometer, in which the amount of electricity to liberate one equivalent of iodine was determined. The Faraday was first determined by means of the silver voltameter.

The value of the Faraday is an important physico-chemical constant, for, as we shall see later, we can calculate from it Avogadro's Number, the number of molecules of a substance in a gram-molecule.

Although it seems so clear, it is surprising that from 1834 until 1881 it remained unnoticed that if Faraday's Laws were true and matter was atomic, electricity, like matter, could not be continuous, but must be discrete, being made up of small units. It was Helmholtz who first pointed this out in his famous Faraday Lecture, delivered before the Fellows of the Chemical Society, in London, on April 5th, 1881. He said: "Now the most startling result of Faraday's Laws is perhaps this. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity."

Thus was born the idea of the "electron"—the atom of electricity. Helmholtz did not use this term. It had, in fact, been stated by G. Johnstone Stoney in 1874, though not published until 1881, that "Nature presents us with a single definite quantity of electricity which is independent of the particular bodies acted upon. To make this clear, I shall express Faraday's Law in the following terms, which, as I shall show, will give it precision, viz.: For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte, which is the same in all cases". The same person gave the name "electron" to this "single definite quantity of electricity" in 1891.

All this, however, was concerned with electrolytes, i.e., solutions of metallic salts in water, and it did not follow that this unit of electricity

had anything whatever to do with the structure of matter. It must be clearly understood that Faraday's Laws lead only to the conclusion that there exists a fundamental unit of electricity, and that this is in some way connected with valency, for a univalent ion bears one, a bivalent ion two, a trivalent ion three, and so on, of these units. It did not show at all that these units enter into the composition of the atom, as we now believe.

The next step in the unravelling of the structure of matter came from

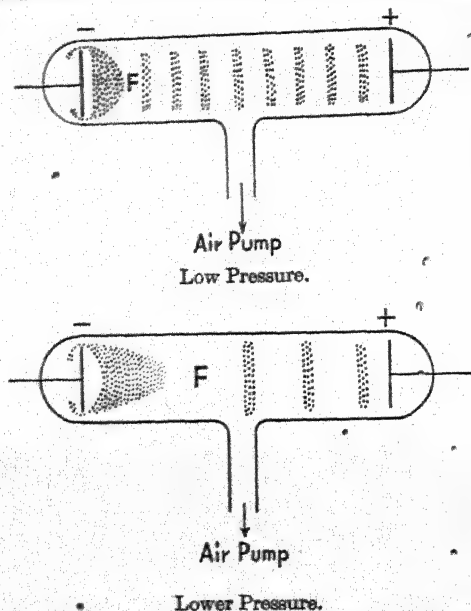


FIG. 16.—Appearance of the Electric Discharge through a Gas.

observations on the conduction of electricity by gases, and the study of radioactivity.

15. The Conduction of Electricity through Gases.—The passage of the electric current through a gas was first studied systematically by Faraday in the years 1836-38. He then appeared to drop this study and did not take it up again until 1858. When a potential is applied to a gas such as air at ordinary atmospheric pressure, the gas behaves as an insulator, and a negligible current passes. If, however, the applied potential is sufficiently high, and the pressure is reduced, a point is reached when a current flows, and the tube is filled with a glow—of a reddish purple colour in the case of air. This is what occurs in the ordinary Geissler tube. If the pressure is still further reduced the glow becomes less symmetrical, a dark space, F (Fig. 16), appearing round the cathode. This is called the Faraday dark space, and is separated from

the cathode by a bluish glow. Between the dark space and the anode is a series of striations, called the positive column. These striations, more than anything else, attracted scientists to study the discharge. Many thought they were something fundamental, and Faraday thought that each striation contained a unit of electricity. Still further reduction of pressure results in the formation of a new dark space immediately round the cathode, and the striations widen out. The state of the discharge in the two instances is shown in Fig. 16. The new dark space round the cathode is called the Crookes space. If the pressure is reduced to about 0.01 mm., the dark spaces and the cathode glow increase in size and the positive column gets smaller, and ultimately the Faraday dark space disappears, as it were, out of the end of the tube, as the positive column has done before it, so that the tube is now entirely occupied by the Crookes dark space and the cathode glow.

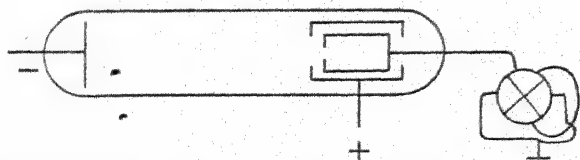


FIG. 17.—Apparatus to show the Nature of the Charge on the Cathode Particle.

There are several things to be noticed about the Crookes dark space. It is always bounded by a luminous area. When the boundary is the gas in the tube the luminous area is the cathode glow, but when the dark space extends to the walls of the tube a bright fluorescence is produced. The colour of this fluorescence depends on the nature of the glass. If a metallic body is placed between the cathode and anode, it will cast a well-defined shadow on the walls of the tube, thus showing that whatever it is that produces this effect is travelling in straight lines. If a miniature paddle wheel is placed in the space, the wheel will rotate, thus showing that whatever is in this dark space will produce mechanical motion. These two facts together make it fairly clear that some sort of radiation is present, and the name *cathode rays* is given to it.

The cathode rays will also produce heating effects; if they strike any object placed in their path they may heat it to redness. If the rays are caught in a hollow metal box placed in the discharge tube, and connected through the wall of the tube to an electrometer (Fig. 17), it is found to gain a negative charge, so that whatever these rays may be, they are accompanied by a stream of negative electricity.

If an external magnetic field is applied to the discharge tube in which the discharge is passing, the cathode rays are deflected from their path in a direction at right angles both to their own path and to the direction of the lines of force of the field. This can readily be shown by passing the

rays through a narrow slit, so that they pass along a zinc sulphide screen, in which they will produce fluorescence. The path of the rays is easily seen. On applying the field, usually by means of an electromagnet, the beam is seen to be bent. Considering the direction of the lines of force, and the direction in which deflection takes place, it follows from the usual rules governing the effect of a magnetic field on a current, that the rays consist of negatively charged particles, if, indeed, they are particles at all. An electrostatic field causes a deflection, but in a different direction. If a cathode particle is moving in the plane of the paper, and a magnetic field is applied with lines of force perpendicular

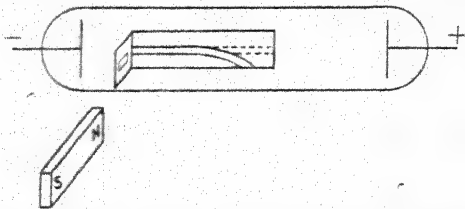


FIG. 18.—Arrangement of Apparatus to show the Deflection of Cathode Rays by a Magnetic Field.

to this plane, the cathode particle will be deflected at right angles to its original path, but still moves in the plane of the paper. When an electrostatic field is applied, with its lines of force perpendicular to the paper, the cathode particle is acted upon by a vertical force, which tends to lift it out of the plane.

The cathode rays will pass through thin pieces of metal, the stopping power of the metal being proportional to the thickness and density. They will act as nuclei for the condensation of supersaturated vapours, causing fogs to be produced.

The nature of the cathode rays was for some time a matter of doubt. Crookes regarded them as a radiant fourth "state of matter", but it was shown by Thomson, by means of experiments about to be described, that the ratio of the charge to the mass of the particle was the same irrespective of the nature of the gas in the tube. It was this observation that first indicated that the cathode rays are common constituents of all atoms.

The experiments of Thomson left no doubt that the cathode particles were actually electrons.

Note on Electromagnetic and Electrostatic Units.—In this chapter we shall have occasion frequently to use electrical units, and it is necessary to be thoroughly acquainted with the relationships that exist between the various systems in common use. There are two systems of *absolute* units—the *electrostatic* (abbreviated to e.s.u., and ultimately based on the force between two electric charges), and the *electromagnetic* (abbreviated to e.m.u., and ultimately based on the magnetic force due to a current). The

absolute units are frequently too small or too large for everyday use, and a system of *practical* units is also used; the practical units are obtained from the corresponding absolute units by multiplying or dividing the latter by powers of 10.

Thus, the ampere and the volt are practical units, being respectively one-tenth of, and 10^8 times the corresponding absolute units on the electro-magnetic system.

When the dimensions of the units on the two absolute systems are compared, it is found that the ratio of the electrostatic to the electro-magnetic unit is a velocity, the reciprocal of a velocity, or the square of a velocity. Calculation reveals that this velocity is none other than the velocity of light, which is usually denoted by c , and is equal to 3×10^{10} cms. per second. In order to convert the electrostatic unit of current into the electromagnetic unit, it will be necessary to divide it by 3×10^{10} .

The Faraday is 96,500 coulombs. The coulomb is a practical unit, and it happens that to bring it to absolute e.m.u. it must be divided by 10. The Faraday is thus 9,650 e.m.u. To convert this into e.s.u., it must be multiplied by 3×10^{10} , giving $28,950 \times 10^{10}$ e.s.u., the value used in § 26.

An important unit of energy is the electron-volt (e.v.). It is the energy acquired by an electron in falling through a potential of 1 volt. As the charge on the electron (§ 26) is 4.802×10^{-10} e.s.u. and the volt is $1/300$ e.s.u. of potential the work done when an electron falls through a potential of 1 volt is $4.802 \times 10^{-10} \times 1/300 = 1.601 \times 10^{-12}$ erg. For practical purposes we use the M.e.v. which is 10^6 electron-volts.

Many difficulties which arise in using the e.m. and e.s. systems of units are overcome by adopting the rationalised metre-kilogram-second (m.k.s.) system of electrical units. This system is becoming increasingly used in text-books of physics.

16. Determination of the Ratio of the Charge to the Mass of the Cathode Particle (e/m).—The determination of this ratio was one of the fundamental observations which paved the way for the modern theory of the structure of the atom. A knowledge of this constant was necessary for measuring the charge of the electron.

It has already been mentioned that since the cathode particles are charged negatively, they are deflected by magnetic and electric fields, and it was this behaviour that was used to obtain the ratio of the charge to their mass. At first, it was possible to determine only the product of the velocity (v) of the particles and e/m . If a magnetic field of strength H is applied transversely to the direction of the rays, they are bent into a circle, the radius (r) of which can easily be determined by causing them to strike a zinc sulphide screen, in which they induce phosphorescence. Suppose the charge on the cathode particle is e , and its mass m , the magnetic force acting on the particles, Hev , must be equal to the centrifugal force mv^2/r . Thus

$$\frac{mv^2}{r} = Hev,$$

or

$$\frac{m}{e} \cdot v = Hr.$$

The next matter was to discover v . It was thought that this velocity would be about the same as that of gas molecules as calculated by the kinetic theory (§ 12f). This incorrect assumption led to a value of e/m which was roughly equal to the value obtained for the hydrogen ion in electrolysis, i.e., 9,650 e.m.u.

Further methods were soon devised for determining e/m and v separately. In the first of these, the cathode particles were deflected by passing through a magnetic field, and were caught in an insulated metal box connected with an electrometer, of which the capacity was known. The rise in potential indicated by the electrometer in a given time was observed, thus giving the total charge, Q , on all the particles which were caught by the box. The total energy, W , of the particles was obtained by causing them to fall on a thermal junction placed inside the hollow box. If N is the number of particles collected in a given time, we have

$$\begin{aligned} Ne &= Q, \\ N \left(\frac{1}{2}mv^2 \right) &= W, \\ \frac{mv}{e} &= Hr. \end{aligned}$$

Eliminating N ,

$$\begin{aligned} v &= \frac{2W}{QHr}, \\ \frac{m}{e} &= \frac{Q}{2W} (Hr)^2. \end{aligned}$$

In this way the two values, that of the velocity of the rays and that of the ratio of their charge to their mass, can be found. The velocity was found to be about one-tenth that of light, and e/m about 10^7 e.m.u. This was about 1,000 times as great as the value obtained for the hydrogen ion in electrolysis; and so it was apparent that the cathode particles probably had small mass, but possessed comparatively high velocity. If it could be assumed that the charge associated with the cathode particle was the same as that carried by a univalent ion in electrolysis it would be possible to calculate m . This assumption could not actually be verified until some time later when the charge on the cathode particle was determined separately. If the assumption was true, the mass of the cathode particle was about one-thousandth of that of the hydrogen atom.

The second method of determining v and e/m separately depended upon the deflection of the rays by both a magnetic and an electric field. The apparatus employed is shown diagrammatically in Fig. 19. Cathode rays from C passed through the two slits A and B, which were earthed, and therefore served as anodes. They made the beam narrow. At the end of the tube was a fluorescent strip upon which the position of the

beam was registered. An electric field was applied between the plates DD. This caused the rays to be deflected from their normal path, and the spot of light moved down the strip. Now, by applying a magnetic field between the plates DD, perpendicular to the path of the rays and parallel to the plane of the plates, the effect of the electric field can be annulled, since the magnetic and electric fields produce opposing deflections of the rays. The spot of light can thus be brought back to its original position. The strengths of electric and magnetic field necessary to do this are obtained. It then follows that, if X is the strength of the electric field, and the other symbols have their former significance.

$$Hev = Xe,$$

or

$$v = X/H.$$

The velocity of the particles thus determined was approximately the same as obtained in the previous determination. The value of e/m could now be determined by applying the magnetic field alone and determining the deflection. As before, this value came out to be about 10^7 e.m.u.

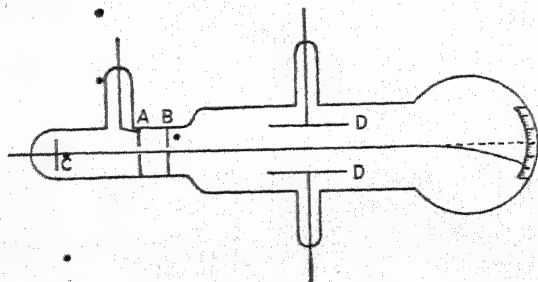


FIG. 19.—Apparatus for determining v and e/m of Cathode Particles.

By varying the gas in the tube, and its pressure, it was found that the velocity of the cathode particles was dependent upon both these factors, but that e/m was unaffected by either alteration. This provided further proof that the cathode particles were constituents of all matter. Numerous other methods have been used for the determination of e/m , and all confirm J. J. Thomson's result, 1.77×10^7 e.m.u.

17. Positive Rays.—Since electrons are charged negatively they are driven away from the cathode in the discharge tube. There are, however, particles which travel towards the cathode from the anode. These eventually strike the cathode and were not discovered until a perforated cathode was used through which they could pass, and their properties could be investigated. For this reason these rays are sometimes called "canal rays" because they have passed through "canals", or perfora-

tions in the cathode. It is found that these rays can be deflected by means of a magnetic field, but the direction of deflection is opposite to that observed in the case of cathode rays, thus indicating that they bear a positive charge; the deflection is also smaller than with cathode rays for the same strength of field, indicating that the particles have a greater mass. These positive rays are of immense importance in elucidating atomic structure.

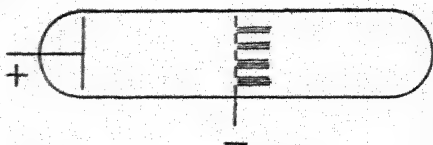


FIG. 20.—Production of Positive Rays.

18. X-Rays.—When cathode rays strike any material object, a new radiation is given off, which has extraordinary powers of penetration, and will affect a photographic plate. For the production of these rays, which are called *X-rays*, a special tube is designed, a simple type of which is shown in the diagram (Fig. 21).

The tube consists of an ordinary discharge tube, which has been exhausted to such an extent that the Crookes dark space fills it. The cathode *C* is made of aluminium and is concave, thus causing the cathode rays to come to a focus at a point *F*, where they impinge on a piece of platinum arranged at an angle of 45° to the axis of the cathode, so that the *X*-radiation emitted at the impact is sent out of the tube. This piece of platinum, which is connected to the anode *A*, is called the anticathode.

More modern types of *X*-ray tube have water-cooled anticathode systems, and the *X*-rays emerge from a window of thin aluminium foil ($\frac{1}{16}$ mm.) placed immediately in front of the anticathode.

The *X*-rays will excite fluorescence in certain substances, and particularly in zinc sulphide and barium platinocyanide. When *X*-rays were first used for examination of bones, etc., it was always the fluorescence effect that was made use of, the shadow of the bones cast on a barium platinocyanide screen being examined. The photographic effect of *X*-rays has, however, proved much more convenient for this, as for most other *X*-ray work. It has the great advantage that long exposures of the affected parts are not required, thus preventing the risk of burning. Also, the *X*-ray photograph obtained can be studied at leisure, and in detail.

X-rays also have the remarkable power of enabling a gas to conduct

electricity after it has been exposed to the rays. Thus, if an aluminium tube containing a gas, and with a wire running through it but insulated from it, is connected with a battery and an electrometer, as shown in Fig. 22, no current flows before the tube is irradiated with X-rays, but as soon as the rays are switched on, the gas becomes conducting.

This is due to the fact that the passage of the X-rays ionises the gas, that is, it causes the gas atoms to become positively charged by the removal of electrons. This phenomenon of the ionisation of gases by means of X-rays is often used when it is necessary to render a gas conducting (as in Millikan's experiment, § 26), and for providing nuclei for the condensation of supersaturated vapours (as in Wilson's experiments, § 21).

X-rays were once considered to be pulses in the ether (*i.e.*, short groups of waves), but they are now known to be a wave motion of extremely small wavelength, about 10^{-8} cm. The wavelength of sodium light is about 5,890 Ångstrom units, one Ångstrom unit being 10^{-8} cm., so that X-rays have a wavelength roughly 5,000 times smaller than that of visible light. The wavelength of the X-rays emitted from any tube depends upon the nature of the anti-cathode. It has been determined by studying the interference of the rays when they fall on a crystal, which acts as a three-dimensional grating for them, just as a diffraction grating is used in optics to determine the wavelength of light. The method of carrying out this experiment is described in the chapter on the Solid State (§ 134). One of the most important uses to which X-rays have been put is the study of crystalline structure.

When X-rays strike other bodies, other X-rays are emitted from these bodies, called secondary rays, whilst some are diffusely reflected. The

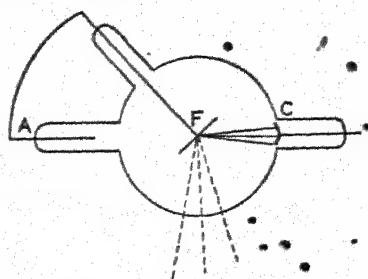


FIG. 21.—X-ray Tube (diagrammatic).

Electrometer

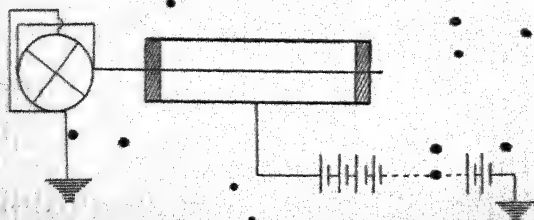


FIG. 22.—Apparatus to show Ionisation of a Gas by X-rays.

secondary rays are made up of two groups: the "K Series", which are of shorter wavelength, and are penetrating, and are called "hard" rays; and the "L Series", which are softer, of longer wavelength, and not so penetrating. The wavelengths of secondary rays are determined by the element on which the impingement takes place, being governed by the atomic number of the element according to a relationship to be discussed later (§ 37). The study of these secondary rays has provided a most important method of deciding atomic structure, and particularly of discovering the number of electrons present in the atom outside the nucleus.

19. Radioactivity.—Shortly after Röntgen's discovery of X-rays in 1895, Becquerel discovered that photographic plates which had been placed near uranium salts were fogged, showing that some penetrating radiation which could affect the plate was emitted by these compounds. The rays were found to be very similar to X-rays in their properties, as they would also ionise gases, and induce phosphorescence in certain substances. They were not affected by heat, light or chemical combination. No matter what uranium compound was used the activity was still present.

Two years later, Mme. Curie found that thorium compounds acted similarly, and investigated also the uranium minerals. Some of these, she found, were more active than uranium itself, so that they must contain a more active element or compound. After a long process of chemical separation, she isolated two other elements which had a much greater activity than uranium. These she called polonium, an element related in chemical properties to tellurium, and radium, which behaves chemically like barium.

Other investigators took up the study of radioactive minerals, and in 1900 another element, actinium, was discovered by Debierne and Giesel.

The sources of uranium and radium salts are minerals, such as pitchblende (which was shown by Klaproth to be an oxide of uranium, U_3O_8), containing a very small amount of radium, and carnotite, a vanadate of potassium and uranium. The latter contains also some radium, and is an important source of the metal. It is much more difficult to obtain radium from mineral sources than it is to get uranium, although radium is always associated with uranium in very small proportions (about 1 gm. of radium in 3 tons of uranium). Uranium salts are comparatively cheap, whilst, of course, radium is the most costly of metals. Unfortunately, the radiation from uranium is not medically active, or at any rate is not sufficiently strong to act in an appreciable time, that of radium being 1,000,000 times as active.

The separation of radium from minerals is a very laborious process, depending upon repeated fractional crystallisation. To obtain it from carnotite, the mineral is heated to 190°C . with about 80 per cent

sulphuric acid; the solution is filtered through glass wool, when, on cooling, it deposits radium and barium sulphates. Radium is a metal of Group II. in the Periodic Table, and resembles barium. Consequently its sulphate is insoluble in water, being, as would be expected, even less soluble than barium sulphate. Both are, however, soluble to a limited extent in strong sulphuric acid, the acid sulphates (e.g., $\text{Ba}(\text{HSO}_4)_2$) being formed. Hence the method adopted for the separation. The sulphates are now reduced to sulphides by heating with carbon, and the sulphides are treated with hydrobromic acid to convert them into bromides. The solution is then crystallised. Eight fractional crystallisations are usually sufficient to effect complete separation.

Radium is a silvery-white metal like barium. The salts resemble those of barium in almost every respect, but in solution oxygen and hydrogen are given off continuously. The dry salts will ozonise air, and in the dark they phosphoresce.

20. Nature and Characteristics of the Radiation from Radioactive Substances.—The radiation emitted from radioactive substances has been shown to consist of three types, which are named α -, β - and γ -rays, and which differ considerably in their nature. They have different penetrating and ionising powers. The α -rays have the lowest penetrating power. The distance they will travel is called their *range*. They will travel for distances of about 7 cm. in air at atmospheric pressure, but they are soon stopped by any solid body, such as a sheet of paper. β -Rays are much more penetrating, and will pass through thin sheets of metal. As for X-rays, the more dense the metal, the greater is its stopping power, and so it is found that β -rays are stopped by lead of greater thickness than about 3 mm. γ -Rays are still more powerfully penetrating, passing through 6 inches of lead.

The nature of these radiations has been elucidated by studying the action of magnetic and electric fields upon them. The effect of a magnetic field on these radiations is shown in Fig. 23. Here it is seen that the effect on α -rays is opposite to that on β -rays, showing that they are opposite in charge. The effect, too, is greater upon β -rays than it is upon α -rays, as can be seen by the greater curvature in the former case. This means that the α -rays have considerably greater mass than β -rays. The γ -rays are quite unaffected by a magnetic field, indicating that they do not possess any electric charge at all. It has been shown that these rays are actually similar in nature to X-rays, but as a rule, have even shorter wavelength. Their wavelength, however, varies, and some γ -rays possess wavelengths of the same order as those of X-rays.

21. α -Rays.—The elucidation of the nature of α -rays was one of the early achievements of Lord Rutherford. He showed that they were positively charged particles, and by determining the ratio of the charge to the mass by a method similar to that used for cathode rays, he showed that their e/m value was 48,230 coulombs per gram. It will be remem-

bered that for the liberation of 1 gm. of hydrogen in electrolysis 96,500 coulombs are required, so that this value is just half that for the hydrogen ion. The α -rays were thus particles which were positively charged and had masses of the order of atomic mass. There are several possibilities: the rays may consist of singly charged atoms with mass 2, or of atoms of mass 4, bearing two positive charges, atoms of mass 6, triply charged, and so on. If they were doubly charged atoms of mass 4, they would consist of helium atoms bearing two positive charges, i.e., the helium nucleus (§§ 29, 35).

This last view was proved to be correct by direct experiment. Rutherford and Royds sealed up some radium emanation (§ 31) in a thin glass tube so that the α -rays could get through the walls. This was

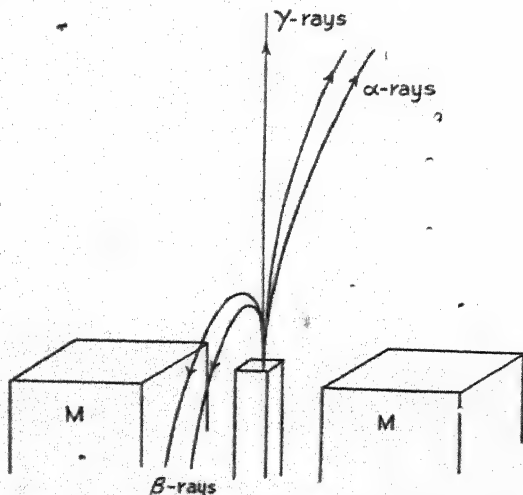


FIG. 23.—The effect of a Magnetic Field on α , β and γ -rays.

placed in an outer evacuated tube fitted with electrodes. On passing the discharge, the spectrum of helium was obtained.

This could be confirmed by determining the charge on the α -particle, and then calculating the mass m from the ratio e/m . There are several ways in which this can be done. When α -rays fall on a zinc sulphide screen they cause phosphorescence, each α -particle causing a definite flash. This has been made use of in the spinthariscopes, an instrument described in § 125, in connection with the determination of Avogadro's Number. It is there described how the α -particles can be counted by noting the number of flashes in a given time. Rutherford determined the number of α -particles falling on a given surface in a given time, and also, in another experiment in which the zinc sulphide screen was replaced by

a metal screen, the charge imparted to the latter in the same time. He was thus able to calculate the charge associated with each α -particle, and this came out to be 9.3×10^{-10} electrostatic units, which is just twice the charge on a hydrogen ion. Since e/m for the α -particle is one-half that for the hydrogen ion, the mass of the α -particle must be four times that of the hydrogen ion, i.e., its mass corresponds to that of the helium atom. The α -particle must therefore be the helium atom bearing two positive charges, or the helium atom less two electrons.

Since the α -particle is emitted with high velocity, and its mass is comparatively large, it possesses considerable kinetic energy, and hence in its passage it is able to pass right through atoms [the explanation of this point will be clear after reading the section on the nuclear theory (§ 29)] with practically no deviation, until its energy becomes spent. Towards the end of its path it may be deflected by coming into contact with the electric field of an atom, and this process of scattering of α -rays in gases proved to be the clue which enabled Rutherford to give a picture of the atom.

The actual path of α -particles through gases has been photographed by the ingenious method originally due to C. T. R. Wilson. When the rays pass through a gas, they ionise it, and the ions formed can then act as nuclei for the condensation of supersaturated vapours. If air, saturated with water vapour and perfectly free from dust is suddenly cooled, no water droplets settle out; the air simply becomes supersaturated with water vapour. If now a radio-active source emitting α -rays is placed in or near the vessel, the paths of the α -rays through the gas are made evident by a line of water droplets, which can be photographed if the vessel is illuminated. The photographs of α -ray tracks obtained in this way (Plate I A.) indicate that α -rays pursue a straight course until very near the end of their tracks, when there may be a deviation from the path, which shortly afterwards ends suddenly. Where the deviation occurs, there is a slight spur, which is due to the recoil of the atom which has collided with the α -particle, and from the direction of this spur and that of the α -particle, the relative masses of the atoms can be calculated approximately.

The tracks of α -rays which can thus be made evident to our senses provide a proof of the existence of single atoms. In watching the track of an α -ray we are really watching the motion of a single charged atom.

22. β -Rays.— β -Rays are more penetrating than α -rays, and are also lighter. They move with a much greater velocity, and have been shown to consist of electrons. The mass of an electron of low velocity is about $1/1,850$ that of the hydrogen atom, as has been shown by the experiments on determination of e/m for cathode rays, and of e . This mass is, however, dependent upon the velocity with which the electron is moving. According to the theory of relativity the mass of a moving

electron becomes infinite when its speed is that of light, and is given, for any other speed, by the equation

$$m = m_0 \left[1 - \left(\frac{v}{c} \right)^2 \right]^{-\frac{1}{2}},$$

where m_0 is the mass when the electron is stationary (the so-called "rest-mass"), m is the mass at velocity v , and c is the velocity of light. The β -particles shot off from radioactive sources have various velocities, but those from radium C have velocities approaching that of light.

The β -particle has a small mass compared with that of an α -particle and consequently possesses much less kinetic energy. It cannot, therefore, cause such extensive ionisation as the α -particle, and is more easily deflected by electric and magnetic fields whether these be applied externally, or whether they be due to atoms in the path of the particle. In consequence, it follows a much more devious path through a gas, as has been shown by the cloud method.

23. γ -Rays.—These, as has already been explained, partake of the nature of X-rays, being extremely penetrating. The wavelength varies with the source. If the wavelength is long enough, it is possible to determine it by interference at crystal faces, just as the wavelength of X-rays is determined (§ 134), but in some cases the wavelength is too small for even a crystal lattice to act as a grating.

24. Secondary Radiation.—In dealing with X-rays it was mentioned that when this radiation comes into contact with other matter, the latter itself gives off X-rays, which are called the secondary radiation. The same thing happens when any of the radioactive radiations strike matter. In general, the secondary radiation is much weaker than the radiation which caused it. γ -rays may produce secondary β -rays, and α -rays may produce both β - and γ -rays. When α -rays are absorbed by matter, a new type of radiation, called δ -rays, is also produced. These are soft β -rays, i.e., electrons with small velocities.

25. Recoil Atoms.—When an α -particle is emitted from a radioactive source, it follows, from the principles of mechanics, that the atom from which the α -particle has been shot must recoil, just as recoil occurs when a rifle is fired. The velocity of recoil is governed by the ordinary principle that the sum of the momenta of the two particles is constant. As radioactive atoms are usually very heavy, having atomic weights about 200, it follows that the recoil velocity will be considerably smaller than the velocity of emission. It will, in fact, be about 1/50th of the latter. This velocity, however, is sufficient to enable the recoil atom to possess the power of causing ionisation. The difference between an α -particle and the recoil atom lies in its range. The α -particle, possessing the greater velocity, will go further than the recoil atom. The recoil atoms therefore act like α -particles which have approached the end of their range.

Recoil may also occur when a β -particle is emitted, but it does not appear that the recoil atom in this case is capable of causing ionisation.

26. Determination of the Charge on the Electron.—Faraday's experiments on electrolysis showed that 1 gm. equivalent of any substance is liberated by the passage of 96,500 coulombs of electricity through the solution. Now, if the substance concerned forms a univalent ion, the equivalent is the same as the molecular weight, so that one gram-molecule of a univalent ion is liberated by 96,500 coulombs, or 9,650 e.m.u. This is equal to $28,950 \times 10^{10}$ e.s.u. (see the section on electromagnetic and electrostatic units, § 15). If n is the number of molecules in 1 c.c. of a gas at N.T.P., one gram-molecule of a substance contains $22,400 n$ molecules, in whatever state it is. Hence, the charge, e , on one univalent ion must be $28,950 \times 10^{10} / 22,400 n$ e.s.u., or the product, ne , is equal to 1.24×10^{10} e.s.u. If we could determine n , we could find the charge on the ion, which we could assume was equal to the charge on the electron; but neither of these quantities can be deduced separately from electrolysis experiments, and in the early attempts to determine e , approximate values of n were used. All that was known about n before the magnitude of the electronic charge was determined was that it lay between 10^{18} and 10^{21} , and hence the value of e was quite uncertain.

The first experiments on the determination of the electronic charge were made by Townsend, and have served as the basis of the most accurate methods of Millikan. It is therefore important to study the history of the methods of carrying out this work.

When newly prepared gases are bubbled through water, electrically charged clouds are formed in many cases. Townsend thought of the idea of determining the charge on a drop in such a cloud, which he assumed to be the charge on the electron. Townsend prepared a cloud, using gases obtained by electrolysis. By means of a quadrant electrometer, the total electric charge per c.c. of gas was determined, and the total weight of the cloud was found by absorbing it in drying tubes and finding the increase in weight. To determine the average charge of a drop, it was necessary to find the weight of one drop, and this was done by finding the rate of fall of the cloud under gravity, and applying Stokes' Law for the velocity of a sphere, moving slowly through a viscous medium, under the action of a constant force. It states that

$$v = 2ga^2\sigma/9\eta,$$

where v is the velocity of the drop under gravity, g is the acceleration due to gravity, a is the radius, σ the density of the drop, and η the viscosity of air.

He could thus calculate the number of drops, and knowing the total charge, and assuming that each drop bore one charge, he was able to determine the charge on each particle. This came out to be 3×10^{-10}

e.s.u. After allowing for the fact that some of the drops in the cloud were charged differently, he gave the corrected value $e = 5 \times 10^{-10}$ e.s.u.

Shortly after the publication of this experiment, Sir J. J. Thomson used the same method to determine the charge on the ions produced in a gas by the passage of X-rays through it. A cloud was formed as in C. T. R. Wilson's experiments, by sudden expansion and resulting cooling of the air, causing the water vapour to condense on the ions. The apparatus is shown in Fig. 24.

The sudden expansion is brought about by pulling down the piston P. The weight of the cloud produced was determined indirectly, by calculation, from the amount of cooling produced, and the densities of saturated water vapour at room temperature and at the lower temperature caused by the expansion. The total charge per c.c. was determined by finding the conductivity of the cloud, measuring the current which flowed when a small electro-motive force was applied between the aluminium cap to the vessel A, and the surface of the water. The size of

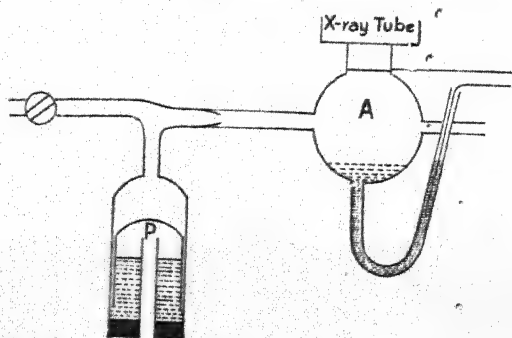


FIG. 24.—Sir J. J. Thomson's Apparatus for determining the charge on the electron (1898).

the drops was determined, as before, by applying Stokes' Law. The values 6.5×10^{-10} e.s.u., and 6.7×10^{-10} e.s.u. were found for the charge on a drop in air, and in hydrogen, respectively. Later, Thomson obtained the value 6.8×10^{-10} e.s.u. for negative ions generated by the action of ultra-violet light. In a later experiment, which he thought to be more accurate, he obtained the value 3.4×10^{-10} e.s.u., using in this case a radioactive source for the ions.

These determinations of Thomson and Townsend were extremely difficult to carry out, and contained numerous sources of inaccuracy. Also, it must be remembered that in all cases it was assumed that each drop was charged with only one elementary charge. That this assumption is very questionable will be clear when the work of Millikan is considered. With his apparatus Millikan was able to obtain oil drops with almost any number of charges. There was also the difficulty that

had to be cleared up, as to whether the charge on these drops was the same as the charge on a univalent ion in electrolysis. Once this had been established, it was possible to find out the size of the charge on the cathode particle, and its mass.

The identity of the charge on the electron and that on a univalent ion was demonstrated by Townsend in 1899. He proved that if e is the charge on an ion in a gas, U its mean velocity in the direction of an electric force Z , and K the coefficient of diffusion of the ions,

$$U/K = neZ/P$$

P being the pressure of the gas, which contains n molecules per c.c., at the temperature of the experiment.

Townsend then determined the coefficient of diffusion of the ions, and, taking the corresponding values of U which had been determined by Rutherford, he obtained the following values of ne (e.s.u.):—

Air	1.35×10^{10}
Oxygen	1.25×10^{10}
Hydrogen	1.0×10^{10}
Carbon dioxide	1.30×10^{10}

The value of the charge on an univalent ion in electrolysis multiplied by the number of ions equal to the number of molecules in 1 c.c. of gas at N.T.P. is 1.24×10^{10} e.s.u. These figures are sufficiently close to the electrolytic value, then, to enable the conclusion to be drawn that the charge on a gaseous ion is equal to that on a univalent ion present in electrolysis, and this has been confirmed by numerous other experiments.

The next development was an improvement made in Thomson's apparatus by H. A. Wilson. The object of it was to avoid the difficulty, already referred to, of the uncertainty as to the number of charges carried by an ion. Two brass plates were fixed in the expansion chamber, A, of Thomson's apparatus, so that a vertical electric field could be applied. It was then possible to aid or hinder the action of gravity on a drop by altering the sign of the electric field. The weight of the drop was determined by the application of Stokes' Law, the rate of fall of the drop under gravity alone being determined. The charge was found from the change in velocity when the electric field was put on to assist the action of gravity. The change in velocity was not the same for all drops the cloud being made up of drops which bore charges in the ratio 1 : 2 : 3.

This important conclusion made it evident that this was a source of inaccuracy in the earlier determinations, though Wilson himself obtained a value 3.1×10^{-10} for the charge on an ion by this method. The idea of using a controlling electric field was worked upon by Millikan, in America, his experiments extending over a period of eight years (1909-16).

Millikan, realising the inaccuracy due to the rapid evaporation of water drops, used instead, drops of a non-volatile oil. He also employed

a much higher field strength, and was therefore able to keep the drop suspended between the plates, or could make it rise or fall at will.

His apparatus is shown in Fig. 25. The oil drops were introduced into the cylindrical vessel V, by means of an atomiser A, resembling somewhat in action a carburetter of a motor car. The brass plates, B and C, were connected, one to the pole of a battery of accumulators, of total voltage 10,000 volts, to maintain a steady high potential, and the other to earth through the vessel. The vessel V was placed in a thermostat to keep it at constant temperature.

The top plate had a pin-hole through which drops of oil occasionally found their way. The drops were already charged by the friction of the

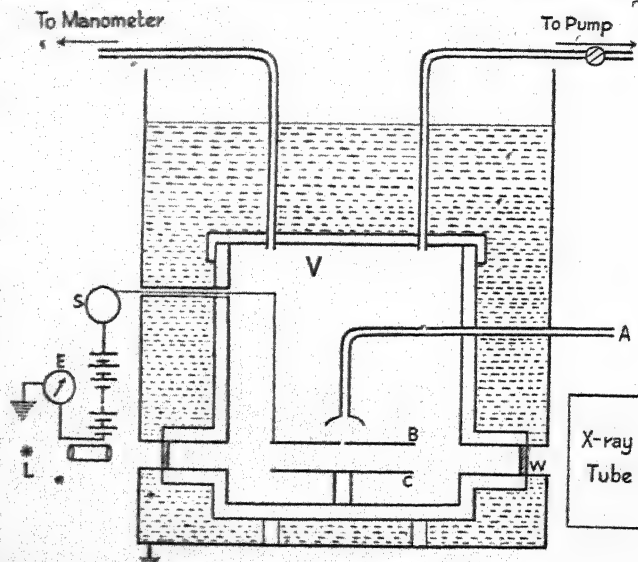


FIG. 25.—Millikan's Apparatus (diagrammatic).

atomiser, but they could be further charged by ionising the gas in the vessel by means of X-rays which were shone through a window, W. The drops which had passed between the plates were illuminated by a powerful source of light, L, and viewed through a telescope. Any heat rays were removed from the light by passing it through filters, so that its entry to the chamber did not upset the motion of the drops by convection currents. The pressure in the chamber, which could readily be altered, was indicated by a manometer. In the telescope eyepiece was a scale which enabled the position of the drop to be gauged to a great degree of accuracy, and the times were recorded to thousandths of a second by means of a chronograph. E was a voltmeter for measuring the potential of the battery.

The drop, which was positively charged by friction, entered the space between the plates, and then the electric field was applied so that it was attracted towards the upper plate B. Just before it got there, the plates were short-circuited by the switch S, and the drop was allowed to fall under gravity until it got almost to C, when the field was put on, and it was dragged up again. The drop could thus be made to rise or fall continuously, and the attainment of another charge was immediately shown by a change in the velocity. The times taken for the drop to fall alone under gravity, and to rise under the action of the field, were found. The time taken for a drop to fall a distance of 0.5222 cm. was 13.595 sec., the maximum deviation in seventeen experiments being only ± 0.2 sec. On the other hand, the times taken for the drop to rise under the action of the field (5,051 volts) varied considerably, as is shown by the following numbers, which represent the times in seconds taken for the upward journey on successive occasions: 12.5, 12.4, 21.8, 34.8, 84.5, 84.5, 85.5, 34.6, 34.8 secs.

It is clear that on the third journey up, the drop had taken up another negative ion, on the next journey another, and on the next, another. If v_1 is the velocity under gravity alone, and v_2 the velocity under gravity and the field of strength X , and e is the charge on the drop of mass m , then

$$\frac{v_1}{v_2} = \frac{mg}{Xe - mg} \quad ; \quad e = \frac{mg}{Xv_1} (v_1 + v_2).$$

The change in velocity consequent upon the drop taking up an additional charge, can be obtained from the equations

$$e = \frac{mg}{Xv_1} (v_1 + v_2),$$

$$e + 1 = \frac{mg}{Xv_1} (v_1 + v_3),$$

where v_3 is the velocity after taking up an additional charge.

With the figures mentioned above,

$$\text{when } t = 34.8 \text{ secs., } v_1 + v_2 = \frac{0.5222}{13.595} + \frac{0.5222}{34.8} \quad (1)$$

$$\text{when } t = 84.5 \text{ secs., } v_1 + v_3 = \frac{0.5222}{13.595} + \frac{0.5222}{84.5} \quad (2)$$

\therefore The difference between (1) and (2)

$$= 0.5222 \left(\frac{1}{34.8} - \frac{1}{84.5} \right) = 0.00891 \text{ cm./sec.}$$

In this way it was found that the successive capture of a single charge by the drop gave rise to differences in its velocity equal to 0.008912, 0.008911, 0.008903, 0.008883, and 0.008931 cm. per sec., giving a mean

value of 0.00891 cm. per sec. It will be seen that the individual results do not differ very greatly from this mean value.

The fact that relationships of this sort were obtained always, irrespective of the nature of the gas in the vessel, or its pressure, or how long the experiment was being conducted, indicates without the faintest doubt that the charges on ions are all the same in value, or are multiples of some fundamental value. This is the best proof of the atomic nature of electricity.

From the above equations, the ratio e/m for the droplets could be found. To determine e , it is now necessary to find m . This can be done by applying Stokes' Law, but Millikan showed that whilst the Law was true for particles of considerable size, for particles of the size of these droplets it ceased to be more than approximately true. He therefore derived a more accurate form of Stokes' Law which would apply to these particles. By this means he was able to find m with a degree of accuracy comparable to that obtainable in the rest of the experiment. Finally, his value for e was $(4.774 \pm 0.005) \times 10^{-10}$ e.s.u.

Several means of ionisation were employed, and in every case the same result was obtained.

The fact that e has been determined with great exactness enables the value of the Avogadro Number, the number of molecules in a gram-molecule of any substance, to be determined with accuracy. In electrolysis it is found that one gram-molecule of a univalent substance is liberated by 9,650 e.m.u. of electricity, or $28,950 \times 10^{10}$ e.s.u. This is equal to N_e , the number of molecules in a gram-molecule multiplied by the charge on an ion. Thus, if we divide this figure by the charge (e) determined by Millikan, we should arrive at Avogadro's Number (N); this comes out to be $6.062 \pm 0.006 \times 10^{23}$. (For further methods of finding Avogadro's number, see § 125.)

The result of the most recent determination of the charge of the electron (Hopper and Laby, 1941) determined by the oil-drop method is $(4.802 \pm 0.001) \times 10^{-10}$ e.s.u. This value agrees with that obtained by Bearden (1941) by the X-ray method.

27. Sir J. J. Thomson's Theory of the Structure of the Atom.—The experiments already described show without doubt that the electron is an integral part of all matter. The cathode rays emitted from all types of matter have the same elementary charge, and the ions produced by all gases possess this charge or else some simple multiple of it. The electron is, therefore, to be found in the atom. All atoms, in the ordinary state, are, however, electrically neutral, and hence there must be some positive charge somewhere in the atom to neutralise the negative charge of the electrons. The nature of this positive charge was not known when the experiments on the determination of e/m for cathode rays were carried out, and the existence of the electron defined.

Sir J. J. Thomson assumed that the electrons moved in "a sphere of

positive electrification". This, of course, was pure hypothesis. By considering the positions taken up by magnetic poles placed in a magnetic field, Thomson showed that the electrons would arrange themselves in rings of eight, which suggested the periodic recurrence of properties in the elements as the atomic weight increases, and thus fitted in with the Mendeleeff Periodic Table (§ 11), which was based on the Law of Octaves. It certainly seemed that the number eight was a magic number as far as the atom was concerned. This arrangement of electrons was later shown to be essentially correct, though by a somewhat different theory.

28. The Bombardment of Matter by α - and β -Rays.—It has already been shown that the β -rays emitted from radioactive substances are electrons moving with various velocities, in many cases high velocities somewhere in the neighbourhood of the speed of light. If matter is bombarded by these small particles, their resultant deflections should give us some information concerning the electrical state of the atoms in matter.

If a parallel beam of β -rays from some radioactive source is passed through a thin metal sheet, such as a piece of aluminium foil, or gold leaf, the beam emerges divergent. This is due to the repulsion of the β -particles by the electrons in the atom, which possess the same electrical sign. From the amount of the divergence, the number of electrons in the atom of the metal can be found. This comes out, as a rule, to about half the atomic weight. Thus, for aluminium it is 13, whilst the atomic weight of aluminium is 27; for sodium it is 11, the atomic weight of this element being 23. Now the mass of the electron can be determined, since we know e/m , and we know e . Its mass is very small indeed. Since an atom like aluminium contains only 13 of these, the proportion of the mass of the atom due to the electrons is very small. The electron has a mass of about $\frac{1}{1850}$ that of the hydrogen atom, so the

13 electrons will weigh about $\frac{13}{1,850}$ units. The ratio of this to the total

mass of the atom is $\frac{13}{27 \times 1,850} = \frac{1}{38,430}$. Hence there must be some

other part of the atom which possesses most of the mass, and since the atom is supposed to be made up of nothing but electricity, it follows that the mass is concentrated in the positive part of the atom.

This view was to receive considerable support from the study of the bombardment of matter by α -particles. These are small, positively charged particles, and are much heavier than β -particles. They will therefore be more effective in bombardment (see § 45).

Geiger and Marsden studied the result of bombarding a piece of gold foil with α -particles from a radioactive source. Some of the particles were deflected slightly from their course, some were scattered through

larger angles, and some were actually deflected right back. The number which suffered a deflection of about 180° was, however, very small, being only about 1 in 20,000. The

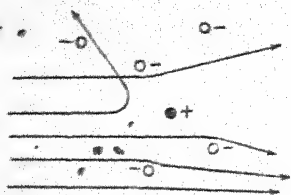


FIG. 26.—The scattering of α -Particles at Electrons and Protons.

average scattering was 0.87° , showing how few suffered anything but a very small deflection. It might be thought that those particles which were directly reversed in direction were merely reflected from the surface of the gold leaf, but this is not so, since the number of particles which undergo large deflections is proportional, within certain limits, to the thickness of the gold foil. It is, therefore,

some phenomenon connected with scattering in the interior of the metal. What is it that causes certain α -particles to suffer such large deflections?

29. The Nuclear Theory of Rutherford.—It was these data which furnished Rutherford with the material upon which to base the nuclear theory of the atom, which, modified and extended, forms the basis of all modern work on subatomic physics.

The α -particle is about 7,000 times as heavy as the electron, so that it will be hardly moved out of its course at all by coming into contact with one of them. As it is turned back through such large angles, it must be colliding with something of about its own mass and charge. Rutherford pointed out that if Thomson's "sphere of positive electrification" were condensed into a small nucleus, the particle necessary to cause these deflections of the α -rays was present. On this basis, Rutherford calculated, from the values of the scattering of α -particles, the number of charges there must be on the positive sphere, and found it to be equal to about half the atomic weight. The charge on the positive sphere, or nucleus, was the same as the total charge on the extra-nuclear electrons in the atom which had been determined by observation of the scattering of β -rays, and later of X-rays. There can therefore be only one of these centres in each atom, otherwise the atom would be positively charged.

Rutherford's theory is that the atom is made up of (1) a positive nucleus, which is small, but which possesses the major part of the mass of the atom; and (2) a number of negative electrons, equal to the number of net positive charges on the nucleus.

It is clear that if these electrons are stationary, there is no reason whatever why they should not be attracted by the nucleus, and fall into it. In order to avoid this difficulty (which was not present in the Thomson model) it was assumed that the electrons moved in orbits round the positive nucleus, being kept from falling into it by the centrifugal force which was always acting outwards.

The atom has often been likened to a solar system in miniature. The

positive nucleus is the sun, the electrons are the planets. If the planets were not in motion round the sun, they would immediately fall into it; but as they are in motion in orbits, the centrifugal force prevents them from being drawn in. This simple picture of the atom provided a very satisfactory method of explaining many facts, but it has now been superseded, as will be described later. Niels Bohr, for example showed that such an atom would be unstable, and modified the model by supposing that the electrons could only move in certain definite orbits (§ 58).

30. Protons, Electrons, and Neutrons.—The name given to the heavy particle bearing one positive charge only, is the *proton*. The hydrogen atom, being the lightest atom, must contain the lightest nucleus, and it is known that it has one extra-nuclear electron. It is possible to obtain, in a suitable discharge tube, positive rays which consist of hydrogen atoms which have been deprived of their electrons, and which therefore consist of a nucleus bearing one positive charge.

The proton is much heavier than the electron, accounting as it does for nearly all the mass of the atom; but it cannot be a very large particle, because so few α -particles are deflected through large angles when matter is bombarded with them. It will be remembered that the total average scattering was only 0.87° , showing that the vast majority of α -particles merely grazed the nucleus, being deflected but slightly by it, whilst very few hit the nucleus head on, and were returned along the path they had come, or nearly so. This means that the spaces in the atom are very large, it being possible for an α -particle, which we know to consist of the helium nucleus, to get right through without hitting anything. In a sheet of aluminium foil, the α -particle may go through thousands of atoms without suffering collision.

In this respect the atom again resembles the solar system. In the latter, by far the greater part of the system consists of empty space, and shooting stars can pass right through it without colliding with anything. The α -particle in the scattering experiments can be likened to a shooting star. It may pass through the atom without hitting anything; on the other hand, it may collide with a nucleus, though the chances of its doing so are small.

The mass of the electron is about $1/1,850$ of that of the hydrogen atom, as has already been shown, so that it is also about that fraction of the mass of the proton.

It should be mentioned that a particle bearing one positive charge, yet possessing a mass much smaller than that of the proton, comparable, indeed, with that of the electron, has also been discovered, and is called the positive electron or positron (§ 51).

When beryllium, and certain other light elements such as lithium and boron, are bombarded with energetic α -rays from polonium, a very penetrating radiation is emitted. This was discovered by Bothe and

Becker in Germany in 1930, who thought at first that it was a very penetrating γ -radiation. In 1932, Curie and Joliot showed that this radiation was capable of expelling high-energy protons from paraffin wax, and later in that year Chadwick determined the number and range of these protons. The results he obtained were inconsistent with the view that the incident radiation was simply a form of γ -ray, and he showed that it was, in fact, composed of uncharged particles with a mass approximately that of the proton. These particles are called *neutrons*, and are considered to be present in the nuclei of all atoms except hydrogen. The mass of the neutron was determined by Chadwick and Goldhaber in 1939 to be 1.00895 on the basis $O = 16$.

31. Radioactive Disintegration.—We are now in a position to study the products of radioactive disintegration, *i.e.*, the products obtained from radioactive substances when α -rays and β -particles are emitted. These products, starting from uranium, actinium and thorium respectively, are given, together with the half-life values of the elements, in Tables III., IV., and V. A number of radioactive elements, artificially produced, fit into a fourth radioactive series.

The term "half-life" requires explanation. The rate of decay of any radioactive substance is governed by the law that the rate of transformation is proportional to the number of atoms N which are left unchanged, *i.e.*,

$$-\frac{dN}{dt} = \lambda N,$$

where λ is the proportionality factor, known as the radioactive decay constant. Integration of this expression gives an exponential function connecting the number of atoms, N_t , left after time t with the number of atoms originally present, N_0 .

$$N_t = N_0 e^{-\lambda t}$$

$$\text{or } \log N_t = \log N_0 - \lambda t$$

$$\therefore \log_e \frac{N_0}{N_t} = \lambda t.$$

It follows that no radioactive element decays away completely, though its concentration may become so small as to be immeasurable. It is therefore useless to take the time of complete disintegration of an element in order to characterise it, for this would be infinity for all of them. The value taken is, then, the half-life period, *i.e.*, the time taken for the element to become half disintegrated. When we say that the half-life period, or, more simply, the period of radium is 1,590 years, we mean that if we start with 1 gm. of radium, by the end of this period it will be reduced to $\frac{1}{2}$ gm. of radium, and some other products.

From the above expression

$$\log_e 2 = \lambda t, \text{ since } N_0 = 2N_t,$$

where t is the half-life.

$$\therefore t = \frac{\log_e 2}{\lambda} = \frac{0.693}{\lambda}$$

32. The Geiger-Nuttall Relationship.—Geiger and Nuttall discovered that the more rapidly an α -radioactive substance decayed the greater was the range of the α -particles emitted. They found that the range, R , was connected with the decay constant, λ , by the equation

$$\log \lambda = A + B \log R$$

The constant A varies from one series to another, but B is the same for all series, viz., 53.9.

33. The Mechanism of α -Disintegration.—In general terms it is reasonable to assume that a heavy nucleus, i.e., one containing a large number of protons and neutrons, will more readily lose α -particles than a light nucleus, but the more rigid investigation of the reason why certain elements are radioactive is not so easy. Gamow applied the principles of wave-mechanics (§ 67) to the problem, and his results are mentioned here because of their important bearing on nuclear transformations to be discussed later (§ 45).

It is known from mechanics that a system is most stable when its potential energy is a minimum. The potential at different distances from the centre of the nucleus is represented by a curve of the type shown in Fig. 27, where the OX axis represents the distance from the centre O of the nucleus, and OY represents the potential. If the nucleus is approached from the right of the diagram, the curve DE represents the change of potential as the nucleus is approached, and as the inverse square law holds the curve is a rectangular hyperbola. This law does not hold, however, for distances very near to the centre, when the potential drops rapidly, reaching a minimum at the centre of the nucleus itself. As we pass through the centre and away to the left the curve is repeated. The portion of the curve BCD is called a potential well.

Consider an α -particle (assumed to be a constituent of the nucleus) with energy OP. It is within the potential energy well, and according to classical mechanics it could never escape from it as its energy is too small to take it over the rim of the potential crater. According to wave-mechanics, however, there is a small but finite probability for the occurrence of events which, according to classical mechanics, could never take place. The wave representing the α -particle is reflected from the walls of the energy crater and forms a sort of stationary wave. This has the power of tunnelling through the energy hill to a certain extent. The higher is the energy of the α -particle the more likely it is to escape; the necessary tunnelling is here shorter than it is lower down in the well. A high probability of escape means that the radioactive

decay constant, λ , is large. Hence α -particles of high energy will also have high values of the decay constant, λ , which is the qualitative statement of the Geiger-Nuttall relationship. Mathematical treatment of the problem shows that the quantitative expression of the relationship also follows from this proposed mechanism.

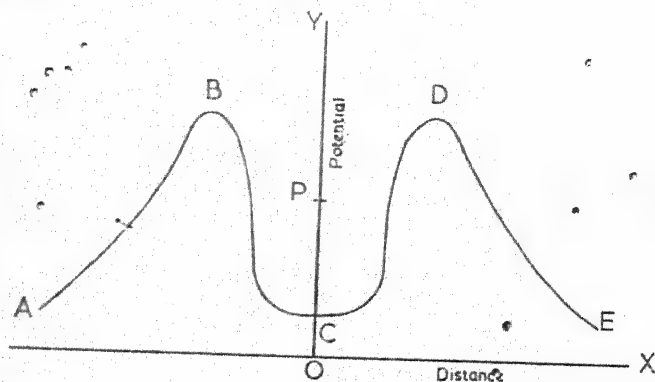


FIG. 27.

The interesting point about the theory is that it indicates that if a nucleus is bombarded with α -rays or protons, some of these may enter the nucleus even if they have not sufficient energy to surmount the energy barrier. They get in by tunnelling through the barrier. It was this suggestion, made by Gamow, that led Cockroft and Walton to carry out experiments on nuclear reactions using bombarding particles of smaller energy than had hitherto been regarded as necessary. These experiments were successful and led the way to the great development of nuclear chemistry that has taken place within recent years.

34. Radioactivity and the Periodic Table.—When an α -particle is emitted by an element, the latter is converted into an element two places to the left in the Periodic Table. Radium in Group II. loses an α -particle, and becomes radon, or radium emanation, a gas of the inert gas series, Group 0. When an element loses a β -particle it changes to one occupying one place to the right. Thus, uranium X_1 , an element in Group IV., loses a β -particle, and becomes uranium X_2 , an element in Group V.

The positions of the various radioactive elements in the Periodic Table are shown in Tables VII.-X.

Now the α -particle consists of the helium nucleus, and bears two positive charges, whilst the β -particle is an electron. It therefore becomes evident that an element A two places to the left of an element B in the Periodic Table must differ from it in possessing two fewer positive charges. The net positive charge on the nucleus of A is two units less than on that of B. Similarly the element B differs from an

element C (formed from it by a β -ray change) in the next place to the right in the Table by possessing one more negative charge on the nucleus, so that when the latter is removed the nucleus increases in charge by 1.

This point is often a troublesome one to grasp. This is not so if it is remembered that it has been shown that both radiations in radioactivity proceed from the nucleus. The β -particle is not an electron removed from the outer sphere of electrons, but one originating in the nucleus. When an unstable nucleus breaks down it does not always emit protons and neutrons, the particles which compose it. It seems that under these circumstances the neutron behaves as if it were made up of a proton and an electron, and the electron is emitted. It is this electron which constitutes a β -particle.

TABLE III.—THE ACTINIUM SERIES

Element.	Symbol.	Radiation.	Half-life Period.	Group in Periodic System.	Atc. No.
Uranium ?	—	α	—	VI.	92
Uranium Y	Uy	β	24.6 hours	IV.	90
Protactinium	Pa	α	3.2×10^4 years	V.	91
Actinium	Ac	—	13.5 years	III.	89
Radio-actinium	Rd-Ac	α (β)	18.9 days	IV.	90
Actinium-X	AcX	α	11.2 days	II.	88
Actinon	An	α	3.92 sec.	0.	86
Actinium A	AcA	α	1.83×10^{-3} sec.	VI.	84
Actinium B	AcB	(β & γ)	36.1 min.	IV.	82
Actinium C	AcC	α	2.16 min.	V.	83
Actinium C'	AcC'	β & γ	4.76 min.	III.	81
Pb ex AcC'	Pb	—	—	IV.	82

TABLE IV.—THE URANIUM SERIES

Element.	Symbol.	Radiation.	Half-life Period.	Group in Periodic System.	Atc. No.
Uranium I	U ₁	α	4.56×10^9 years	VI.	92
Uranium X ₁	UX ₁	β	24.5 days	IV.	90
Uranium X ₂	UX ₂	$\beta (\gamma)$	1.14 min.	V.	91
Uranium II	U ₁₁	α	2.7×10^5 years	VI.	92
Ionium	Io	α	8.3×10^4 years	IV.	90
Radium	Ra	$\alpha (\beta \text{ \& } \gamma)$	1,590 years	II.	88
Radon	Rn	α	3.82 days	0.	86
Radium A	RaA	α	3.05 mins.	VI.	84
Radium B	RaB	$\beta (\gamma)$	26.8 mins.	IV.	82
Radium C	RaC	99.97 per cent. β & γ	19.7 mins.	V.	83
Radium C'	RaC'	α	10^{-8} sec.	VI.	84
Radium D	RaD	$(\beta \text{ \& } \gamma)$	22 years	IV.	82
Radium E	RaE	β	5.0 days	V.	83
Radium F (Polonium)	RaF Po	$\alpha (\gamma)$	140 days	VI.	84
Radium Ω (Lead)	Ra Ω Pb ²⁰⁸	—	—	IV.	82
Radium C	RaC	0.03 per cent. α	—	V.	83
Radium C''	RaC''	β	1.4 min.	III.	81
Radium Ω'' (Hypothetical)	Ra Ω''	—	—	IV.	82

TABLE V.—THE THORIUM SERIES

Element.	Symbol.	Radiation.	Half-life Period.	Group in Periodic System.	Atc. No.
Thorium . .	Th	α	1.39×10^{10} years	IV.	90
Mesothorium I .	↓ MsTh ₁	—	6.7 years	II.	88
Mesothorium II .	↓ MsTh ₂	β & γ	6.13 hours	III.	89
Radiothorium .	↓ RaTh	α (β)	1.90 years	IV.	90
Thorium X .	↓ ThX	α	3.64 days	II.	88
Thoron . .	↓ Tn	α	54.5 sec.	0.	86
Thorium A .	↓ ThA	α	0.16 sec.	VI.	84
Thorium B .	↓ ThB	β & γ	10.6 hours	IV.	82
Thorium C .	↓ ThC	65 per cent. β	60.5 mins.	V.	83
Thorium C' .	↓ ThC'	α	3×10^{-7} sec.	VI.	84
Thorium D .	↓ ThD	—	—	IV.	82
(Thorium-lead)	Pb ²⁰⁸				
Thorium C .	↓ ThC	35 per cent. α	—	V.	83
Thorium C'' .	↓ ThC''	β & γ	3.1 mins.	III.	81
Thorium Ω '' .	↓ Th Ω ''	—	—	IV.	82
(Lead)	Pb ²⁰⁸				

The fact that when these radioactive changes take place they are accompanied by simple moves in the positions of the elements in the Periodic Table is very easily explained by supposing that each element in the Table differs from the one before it by possessing one more net positive charge in the nucleus and one more electron in the extra-nuclear structure. Indeed, this explanation is demanded by the facts quoted above.

ATOMIC STRUCTURE—PART I

TABLE VI.—The Uranium Series.

0	I	II	III	IV	V	VI	VII	VIII
				Ra B α Ra C' (81) β Po ex Ra C' (82)	Ra A α Ra C-β α Ra E-β α U ₂ (90) β U ₂ (91) α U ₂ (92)	Ra A α Ra C' α Ra F (Po) α U ₂ (92)		
Ra (88)	Ra (88)							

TABLE VII.—The Thorium Series.

0	I	II	III	IV	V	VI	VII	VIII
				Th B α Th C' β Po ex Th C' (82)	Th A α Th C-β α Th E-β α U ₂ (90) β U ₂ (91) α U ₂ (92)	Th A α Th C' α Th F (Po) α U ₂ (92)		
Th (90)	Th X (86)							

TABLE VIII.—The Actinium Series.

0	I	II	III	IV	V	VI	VII	VIII
				Ac B α Ac C' β Po ex Ac C' (83)	Ac A α Ac C-β α Ac E-β α U ₂ (90) β U ₂ (91) α U ₂ (92)	Ac A α Ac C' α Ac F (Po) α U ₂ (92)		
Ac (89)	Ac X (88)							

TABLE IX.—THE RADIOACTIVE ELEMENTS IN THE PERIODIC TABLE

0	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
—	—	—	AcC ⁶	AcB. ThB	AcC	AcA	—	—
—	—	—	RaC ⁶	RaB. ThD	RaC	RaA	—	—
—	—	—	ThC ⁶	RaD	RaE	RaC ⁶	—	—
—	—	—	—	Pb Ex RaC ⁶	ThC	RaF(Po)	—	—
—	—	—	—	Pb Ex RaF	—	ThA	—	—
—	—	—	—	Pb Ex ThC ⁶	—	ThC ⁶	—	—
—	—	—	(81)	Pb Ex AcC ⁶	(83)	(84)	—	—
—	—	—		(82)			—	—
Ac	—	AcX	Ac	UY	UX ⁶	U	—	—
Ra	—	Ra ⁶	MsTh ₂	Rd Ac	Pr	UX ₁	—	—
Th	—	MsTh ₁	—	UX ₁	—	—	—	—
—	—	ThX	—	Io	—	—	—	—
—	—	—	—	Th	—	—	—	—
(86)	—	(88)	(89)	Rd Th	(91)	(92)	—	—
				(90)			—	—

Atomic numbers in parentheses.

This theory was put forward quite early by van den Broek (1911), but at the time there was very little evidence to support it, and it was not given much attention. When, however, the place changes which occur during radioactive disintegration were discovered in 1913, the theory was a necessary consequence.

At first the theory was applied only to the radioactive elements, no evidence having been gathered to prove its truth in the case of the lighter elements. This was obtained later by Moseley (1913-14), who examined the X-ray spectra of the elements. If the elements are arranged in the order in which they appear in the Periodic Table, allowance being made for the unknown elements, for which gaps are left, and they are then numbered in order, starting with hydrogen as 1, and ending with uranium as 92, the numbers assigned to each element will represent the number of electrons outside the nucleus (called extra-nuclear electrons), and also the resultant positive charge on the nucleus. This number is called the *atomic number* of the element. Moseley was able to determine the atomic numbers of many of the lighter elements. This work will be described in a later section (§ 37).

35. The Nature of Atoms.—We have seen that the nuclear theory of the structure of matter demands that the atom should contain a nucleus, positively charged, the system as a whole being electrically neutral because of the negative electric charges of a cloud of electrons which surrounds it. The number of these electrons outside the nucleus is the atomic number of the atom. The nucleus itself contains neutrons (§30) as well as protons. So long as the resultant charge of the nucleus is positive, and the number of extra-nuclear electrons is sufficient to neutralise this charge, the conditions for the formation of a normal atom are satisfied.

Take, for example, the atom of helium. The mass of any atom is largely accounted for by the nucleus, the electrons being so light as to be negligible when approximate atomic weights are considered. The atomic weight of helium is about 4. This means that there must be four particles with the mass of the proton in the atom. But its atomic number is only 2, and the nucleus has therefore a resultant positive charge of 2 units, and must contain two neutrons. This positive charge is neutralised by the two extra-nuclear electrons. The helium atom can therefore be pictured as in Fig. 28.

Take as a further example the sodium atom. Its atomic number has been found to be 11. It follows that there are 11 electrons outside the nucleus. The atomic weight is 23, so that the atom must contain 23 particles of unit mass, either protons or neutrons. If it is to be electrically neutral, there must be 12 neutrons and 11 protons in the nucleus. The arrangement of the 11 extra-nuclear electrons has been shown, by methods to be outlined in the next chapter, to be in rings

containing 2, 8, and 1 electron. The simplified model of this atom is drawn in Fig. 29.

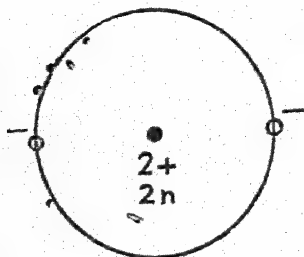


FIG. 28.—The Helium Atom Model (simplified).

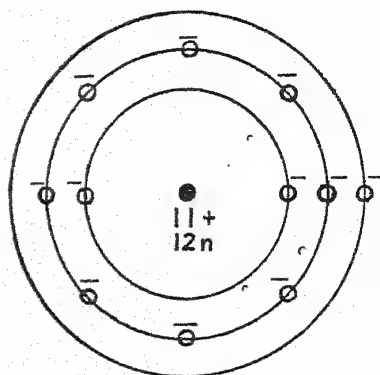


FIG. 29.—The Sodium Atom Model (simplified).

36. The Nature of the Nucleus.—We have already stated that in the nucleus there are protons and neutrons. The arrangement of these particles in the nucleus is even now not correctly known. The fact that α -particles are emitted from atoms seems to show that these must be ready made in the nucleus. Exactly how the neutron is to be regarded is a matter of some doubt. It may be thought of for some purposes as a proton and an electron fused together.

It is obvious that the number of protons in the nucleus is equal to the number of extra-nuclear electrons, and therefore to the atomic number, Z . Since the proton has a mass of approximately 1 unit (the normal hydrogen atom contains one proton and one electron, and the mass of the electron is very small compared with that of the proton) and the neutron also has a mass of approximately 1 unit, the masses of all nuclei are approximately whole numbers. This whole number is called the mass number, A . The number of neutrons, N , in the nucleus is clearly equal to $A - Z$.

The forces holding protons and neutrons together in the nucleus are not yet fully understood, but it is known that only certain numbers of these particles can exist together in a stable nucleus. If these numbers are increased artificially by bombardment with neutrons or protons, and their capture by the nucleus, an unstable nucleus is formed, which will later break down to a stable one. However, for a given mass number there are several possible arrangements of protons and neutrons which will give stability. The same is true for a given atomic number, so that altogether over 250 stable nuclei are known, although the number of chemically identifiable elements is less than 100.

Nuclei with the same mass number and different atomic number are called isobares; those with the same atomic number but different mass number are called isotopes. These topics will be more fully dealt with in § 38.

37. Atomic Numbers and their Determination by Moseley's Method.—

—When an element is bombarded with electrons, X-rays are emitted which are characteristic for the element bombarded. Moseley examined the spectra of the X-rays thus emitted.

The substance under investigation was made the anticathode in a discharge tube. The wavelengths of the X-rays given out were determined by diffraction at a crystal, an X-ray spectrometer similar to that employed by the Braggs in the investigation of crystal structure being used (§ 134). The spectrum was photographed.

The X-ray spectra of the elements are on the whole very simple, consisting of very few lines. In Fig. 30 are shown the spectra of some elements which are adjacent in the Periodic Table. It is seen that the

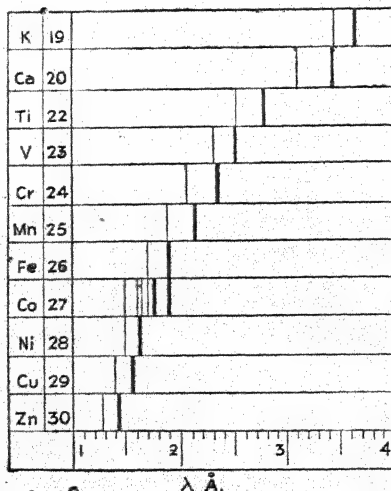


FIG. 30.—X-ray Spectra (*K* series).

spectra are all alike. They all consist of two lines,¹ one being much stronger than the other. Also, all that is necessary to obtain one spectrum from that of the neighbouring element is to shift it a certain distance to the right or to the left according as whether the one element comes after, or before the other in the Periodic Table.

¹ With the exception of cobalt, for which the spectrum is a little more complicated.

Three sets of lines were found, which were called the *K*, *L* and *M* lines, the *K* lines being of the shortest wavelength. They are given by all elements. The *L* series is of longer wavelength and has only been found with elements of atomic weight greater than that of neon (*i.e.*, sodium onwards). The *M* radiation, of longer wavelength still, has only been obtained with the very heavy elements. There are four lines in the *K* spectrum, which appear as two sets of two, the lines in each set being very close together, forming what is known as a doublet. An *N* series probably also exists.

Moseley showed that the frequency of a given line in the spectrum was connected with the atomic number of the element by the simple expression

$$\nu = a(N - b)^2,$$

where ν is the frequency, N the atomic number, and a and b are constants. For the first line (longest wavelength) of the *K* spectrum, known as the $K\alpha_1$ line, the constant a is 2.47×10^{15} , and b is 1. This equation is a linear one, and if ν is plotted against N , a straight line should be obtained. That this is the case is shown by the curves for the three types of spectra (*K*, *L* and *M*) given in Fig. 31.

This work showed the fundamental nature of atomic numbers, and enabled the positive charge on each element to be determined. The work also confirmed the arrangement of the elements in the Periodic Table. It will be remembered that if the elements are arranged in the order of their atomic weights there are several anomalies in the Table. Thus, tellurium comes after iodine, when it is clear from its chemical properties that it should come before. Argon comes after potassium, and since this does not agree with the properties of the elements, they are put out of order in the Table. This alteration was justified by the determination of the atomic numbers of these elements, which indicated that those of tellurium and iodine were 52 and 53 respectively, and of argon and potassium 18 and 19 respectively. The atomic numbers of iron, cobalt and nickel came out to be 26, 27 and 28 respectively, the sequence agreeing with the chemical properties of these elements, but disagreeing with the sequence of their atomic weights. Protactinium and thorium are also now known to be out of order, as far as atomic weight is concerned, but correct with regard to atomic number. The total number of elements from hydrogen to uranium was shown by this work to be 92, and thus the number of rare-earth elements, which could not be satisfactorily defined by the Periodic Table alone, was fixed.

38. Isotopes.—When a radioactive element loses a β -particle its atomic number increases by 1, and so a new element is formed which is one place higher in the periodic system (§ 35). The loss of the very light β -particle entails, however, practically no loss in mass, so the new

element has the same atomic weight as the old. We thus have two elements in the Periodic Table which have the same atomic weight yet differ in atomic number, and in chemical properties. Elements of this type are called *isobares*.

When a radioactive element loses an α -particle, its atomic number is reduced by two and the new element formed occupies a position two places further down the Table (§ 31). If now the new element loses two β -particles successively, the element produced will have the same atomic number as the original one before the series of changes was commenced. The atomic weight, however, will be 4 units less, and so we have two elements occupying the same place in the Periodic Table, yet differing in atomic weight. The chemical properties of such elements are found

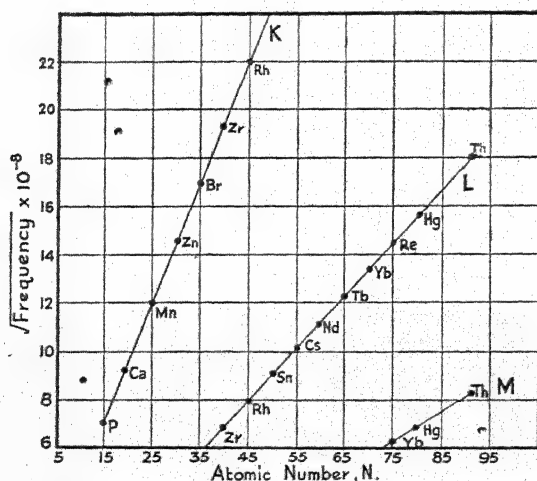


FIG. 31.—Relationship between Frequency of Lines in X-ray Spectra and Atomic Number.

to be almost exactly the same. Indeed, they are so much alike that it is very difficult to separate them. Such elements are called *isotopes*.

The atomic number is the number of extra-nuclear electrons, and also the numerical value of the positive charge on the nucleus. It is clear that isotopes possess the same atomic number, and therefore the same number of extra-nuclear electrons, and consequently the same positive nuclear charge. How then do they differ? We have seen previously that the nucleus consists not only of protons, but also of some neutrons. It is in the number of neutrons in the nucleus that isotopes differ. The chemical properties of an atom are known to depend almost entirely

on the number of extra-nuclear electrons, and as these are the same in isotopes the chemical properties of isotopes of a given element must be almost identical. Only in the case of hydrogen, where the ratio of the isotopic weights is exceptionally high is there an appreciable difference.

It was in connection with the radioactive elements that isotopes were first discovered, but it is now known that they are by no means confined to these elements. Nearly all the elements are now known to be isotopic. When any so-called element is prepared in the laboratory, a pure substance is not obtained, but a mixture of atoms of different atomic weights. The proportions in which these isotopic atoms are present, whenever an element is prepared, are always the same, and so the atomic weight appears to be constant (except in the case of hydrogen, § 43). Thus chlorine consists of two isotopes, of atomic weights 35 and 37. Whenever chlorine is prepared in the laboratory the proportions of these isotopes present are the same. Hence, whenever the atomic weight of chlorine is determined the same result is obtained.

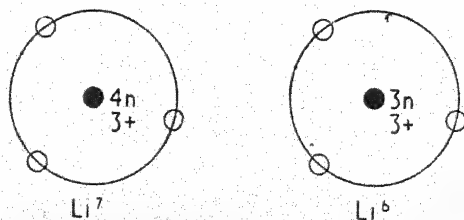


FIG. 32.—Structure of Lithium Isotopes (simplified).

The existence of isotopes can be explained if the possible arrangements of the charges in an atom of an element are considered. To take a simple case, that of lithium, of which the atomic number is 3; there are two isotopes of masses 7 and 6, the former being the predominant one, as can be understood from the fact that the atomic weight of lithium is 6.940. Since the atomic number of both the isotopes of this element is 3, there must be three extra-nuclear electrons. The atomic weight of one of them is 7, hence there must be 7 particles of unit mass in this element. It follows that there must be four neutrons. The atomic weight of the other is 6, and the number of neutrons must be 3. Hence we have two elements with the same atomic number, but with different atomic weights. The properties of the element, being governed by the number of extra-nuclear electrons, are the same in each case, and it would be impossible to distinguish between them chemically. Physically there should be slight differences. For example, the densities of the two forms should be slightly different. It is very difficult to separate isotopes on

the large scale, but the task has been carried out in connection with atomic energy projects, although at great expense.

The usual method of denoting any particular isotope symbolically is by placing the mass-number of the isotope to the top left-hand side of the chemical symbol. Thus ^{17}O means the isotope of oxygen of mass 17.

Prout's hypothesis, which stated that the atomic weights of all elements were multiples of that of hydrogen, has received striking confirmation from modern work on the structure of matter. We now believe that all elements are made up of protons, neutrons, and electrons, and since hydrogen, the simplest element of all, is made up of one proton and one electron, it is obvious that it is correct to regard all elements as made up on the hydrogen type.

Moreover, the masses of all isotopes are very nearly whole numbers and so here again Prout's hypothesis receives confirmation. It is indeed remarkable that this old hypothesis, which was discredited during last century, should turn out to be true after all, though in a very different way from that thought of by its propounder.

The existence of isotopes of oxygen, of mass 17 and 18, raises the question of the suitability of the oxygen atom as a standard of reference for atomic weights. It has been argued that the oxygen isotope of mass 16 should be taken as standard, but this would make direct comparison, by the usual methods of determining atomic weights, impossible. The proportion of the ^{17}O isotope in the ordinary mixture is very small. It has been shown that the ratio of atomic weights calculated on the basis $\text{O} = 16$ to those calculated on $^{16}\text{O} = 16$ is only 1.00027 to 1. Actually the standard $\text{O} = 16$ is used for chemical determinations, and $^{16}\text{O} = 16$ in the physical methods (§ 41).

The preparation of almost pure ^{35}Cl by the method of thermal diffusion (§ 42) has led to the suggestion that when the pure isotope is obtained it should be used instead of oxygen to determine the conversion factors for chemical and physical atomic weight scales.

39. The Detection of Isotopes. Positive-ray Analysis.—The nature and method of production of positive rays have already been briefly mentioned (§ 17). It is by a study of the positive rays emitted from elements that our knowledge of the number of isotopes present in the common elements has been derived.

The first experiments with positive rays which led to important results were made by Sir J. J. Thomson, 1910-12. His apparatus is shown in diagrammatic form in Fig. 33.

The discharge tube *A* was provided with an aluminium anode *D*, and the gas under investigation was drawn in through the fine capillary *E*. The cathode, *B*, again of aluminium, surrounded a brass capillary tube, which was water-cooled by the water-jacket *C*. This tube acted as the perforated cathode, the positive rays passing through it. The positive

rays were made to pass through a magnetic field provided by an electro-magnet with soft-iron pole pieces *MM*, separated from the former by thin pieces of mica, *NN*. Two soft-iron shields, *II*, prevented the electro-magnet from affecting the discharge. An electric field could also be applied. The positive rays after this treatment entered the evacuated vessel *G*, and were recorded on a photographic plate.

The simultaneous action of the electric and magnetic fields caused the positive rays to give rise to parabolas on the photographic plate, and for this reason the method is called Thomson's parabola method. The deviation is dependent upon both the charge and the mass of the particles (§ 16). By comparing the positions of these parabolas on the plate with those due to elements of known atomic weight it was possible to estimate the atomic weight of the element producing them. A line was found due to an element of atomic weight 22. No such element was known. It was at first thought that it was due to carbon dioxide bearing two positive charges (thus giving the effect of an element of mass 22 with one positive charge), but the line did not disappear when

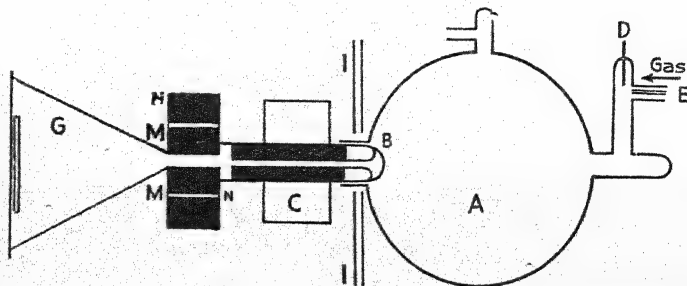


FIG 33.—Sir J. J. Thomson's Positive Ray Apparatus (diagrammatic).

the gas was slowly passed through liquid air, whereas that at 44 due to a singly charged carbon dioxide molecule, did disappear. It was also thought that a compound of neon and hydrogen might be formed of the composition NeH_2 . This would have given the required line, but no evidence of the existence of such a compound outside the tube could be found.

Sir J. J. Thomson considered that he had discovered a new element, and Aston set out to separate the new gas from neon by repeated fractionation with charcoal at the temperature of liquid air, and also by fractional diffusion. After a great deal of work he was able to separate two fractions having molecular weights 20.15 and 20.28 with respect to oxygen as 16 (§ 5). The differences between these two values were too great to account for as experimental error. The two fractions, however, had the same spectra, the same boiling points, and, as far as could be

judged, the same chemical properties. Soddy considered that the two elements, of atomic weights 20 and 22, were isotopes, this being the first example of their existence outside the radioactive elements.

Aston now set out to discover more about these elements of mass 20 and 22, and discarded Thomson's parabola method in favour of an arrangement capable of giving more accurate results, called the mass-spectrograph. The arrangement of the apparatus is shown in diagrammatic form in Fig. 34. *B* is the discharge tube, *A* the anode, and *C* the cathode which has a slit S_1 . A second slit, S_2 , is provided to cut down the rays to a fine parallel beam. This passes between the plates J_1J_2 by which the electric field is applied. The beam now passes through a stop-cock *L*, into the camera part of the apparatus. *M* is a large electro-magnet, by means of which a magnetic field can be applied, at right angles to the electric field. When both fields are applied, the particle

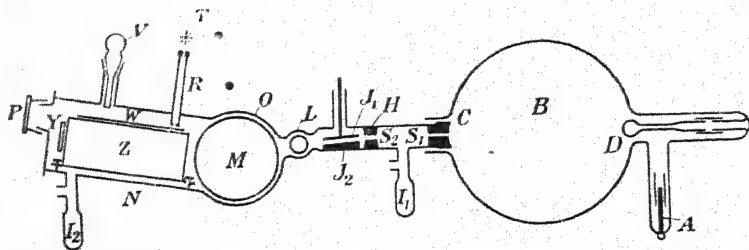


FIG. 34.—Aston's Mass-Spectrograph (diagrammatic). From Aston's "Mass Spectra and Isotopes" (1933), by permission of Messrs. Edward Arnold & Co.

are deflected in the plane of the paper by an amount depending upon the ratio e/m . The rays fall on the photographic plate *Y*, and their positions are measured. The lines obtained are fairly broad, owing to the width of the slit, but the edge is sharp, and this is taken as the position of the line.

Of course, a standard of measurement is required, and for this oxygen is taken. Lines are obtained at positions corresponding to 32, 16 and 8, due to the molecule, the singly charged atom, and the doubly charged atom of oxygen, respectively. By adding carbon dioxide to the tube, lines are obtained at 6, 12, 28 and 44, being due to C^{++} , C, CO and CO_2 respectively, thus providing a number of standards by which to measure the lines produced by other elements.

When neon was introduced into the tube, lines were obtained at 22, 20, 11 and 10. There could be no further doubt that neon was not a pure element, but made up of two isotopes, of atomic weights 22 and 20. Isotopes of chlorine and argon were also found.

This apparatus was only applicable for gases, and it soon became important to discover whether isotopes of the solid elements also existed. For this purpose Aston devised the method of the "accelerated anode ray", in which the positive rays were produced by coating the anode with a suitable salt mixture, containing the element to be tested. Positive ions are emitted and are accelerated in their passage to the cathode, and can then be treated as positive rays. In this way the majority of the elements have been examined.

The existence of isotopes can be shown, and their masses determined, by means of a different apparatus, devised by Dempster (1918) and shown diagrammatically in Fig. 35. In this the positive particles

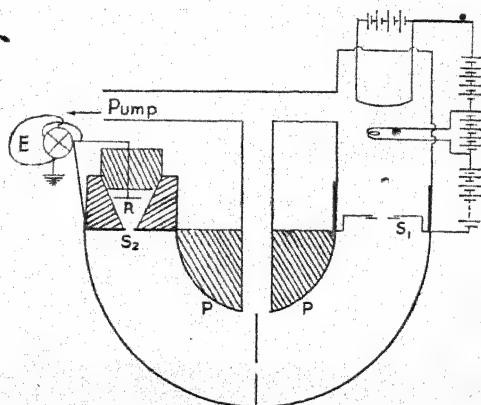


FIG. 35.—Dempster's Positive Ray Apparatus (diagrammatic).

obtained by heating salts on a platinum strip, or by bombarding compounds containing the element under investigation by electrons, are passed through a definite potential difference, and then pass through a slit, S_1 , into the analysing chamber where they are acted upon by a strong magnetic field, bending them into a semicircle. They then pass through a further slit, S_2 , and fall on a plate, R , connected with an electrometer, E . The potential required to bring a particle of known mass on to the detecting electrometer is measured. Actually, the potential is varied, the magnetic field being kept constant, and the ionic current produced in the electrometer is measured. This shows peaks when the particles fall on the plate, the maxima corresponding to particles of definite masses, which can be obtained after standardising the instrument.

Almost all elements have been shown to have isotopes. The Table below (Table X.) gives a list of stable isotopes.

TABLE X.—TABLE OF ISOTOPES

The isotopes are given in the order of their abundance in the elements. Radioactive isotopes produced artificially are not included in this list.

Atomic No.	Element.	Atomic Wt.	Isotopes.
1	Hydrogen .	1.0081	1, 2, 3
2	Helium .	4.003	4, 3
3	Lithium .	6.940	7, 6
4	Beryllium .	9.02	9
5	Boron .	10.82	11, 10
6	Carbon .	12.010	12, 13
7	Nitrogen .	14.008	14, 15
8	Oxygen .	16.000	16, 18, 17
9	Fluorine .	19.00	19
10	Neon .	20.183	20, 22, 21
11	Sodium .	22.997	23
12	Magnesium .	24.32	24, 25, 26
13	Aluminium .	26.97	27
14	Silicon .	28.06	28, 29, 30
15	Phosphorus .	31.02	31
16	Sulphur .	32.066	32, 34, 33
17	Chlorine .	35.457	35, 37
18	Argon .	39.944	40, 36, 38
19	Potassium .	39.096	39, 41, 40
20	Calcium .	40.08	40, 42, 43, 46, 48
21	Scandium .	45.10	45
22	Titanium .	47.90	48, 46, 47, 49, 50
23	Vanadium .	50.95	51
24	Chromium .	52.01	52, 53, 50, 54
25	Manganese .	54.93	55
26	Iron .	55.84	56, 54, 57, 58
27	Cobalt .	58.94	59, 57
28	Nickel .	58.69	58, 60, 62, 61, 64
29	Copper .	63.54	63, 65
30	Zinc .	65.38	64, 66, 68, 67, 70
31	Gallium .	69.72	69, 71
32	Germanium .	72.60	74, 72, 70, 73, 76
33	Arsenic .	74.91	75
34	Selenium .	78.96	80, 78, 76, 82, 77, 74
35	Bromine .	79.916	79, 81
36	Krypton .	83.7	84, 86, 82, 83, 80, 78

Atomic No.	Element	Atomic Wt.	Isotopes.
37	Rubidium	85.48	85, 87
38	Strontium	87.63	88, 86, 87, 84
39	Yttrium	88.92	89
40	Zirconium	91.22	90, 92, 94, 91, 96
41	Niobium	93.3	93
42	Molybdenum	95.95	98, 96, 95, 92, 94, 100, 97
43	Masurium	?	
44	Ruthenium	101.7	102, 101, 104, 100, 99, 96, 98
45	Rhodium	102.91	103, 101
46	Palladium	106.7	106, 108, 105, 110, 104, 102
47	Silver	107.880	107, 109
48	Cadmium	112.41	114, 112, 111, 110, 113, 116, 106, 108
49	Indium	114.76	115, 113
50	Tin	118.70	120, 118, 116, 119, 117, 124, 122, 112, 114, 115
51	Antimony	121.76	121, 123
52	Tellurium	127.61	130, 128, 126, 125, 124, 122, 123, 120
53	Iodine	126.92	127
54	Xenon	131.3	132, 129, 131, 134, 136, 130, 128, 124, 126
55	Cæsium	132.91	133
56	Barium	137.36	138, 137, 136, 135, 134, 130, 132
57	Lanthanum	138.92	139
58	Cerium	140.13	140, 142, 136, 138
59	Praseodymium	140.92	141
60	Neodymium	144.27	142, 144, 146, 143, 145, 148, 150
61	Illinium	?	
62	Samarium	150.34	152, 154, 147, 149, 148, 150, 144
63	Europium	152.0	153, 151
64	Gadolinium	156.9	156, 158, 155, 157, 160, 154, 152
65	Terbium	159.2	159
66	Dysprosium	162.46	164, 162, 163, 161, 160, 158
67	Holmium	163.5	165
68	Erbium	167.2	166, 168, 167, 170, 164, 162
69	Thulium	169.4	169

Atomic No.	Element.	Atomic Wt.	Isotopes.
70	Ytterbium .	173.04	174, 172, 173, 176, 171, 170, 168
71	Lutecium .	175.0	175, 176
72	Hafnium .	178.6	180, 178, 177, 179, 176, 174,
73	Tantalum .	180.88	181
74	Tungsten .	183.92	184, 186, 182, 183, 180
75	Rhenium .	186.31	187, 185
76	Osmium .	190.2	192, 190, 189, 188, 187, 186, 184
77	Iridium .	193.1	193, 191
78	Platinum .	195.23	195, 194, 196, 198, 192
79	Gold .	197.2	197
80	Mercury .	200.61	202, 200, 199, 201, 198, 204, 196

Atomic No.	Element.	Atomic Wt.	Isotopes.	Radioactive Isotopes.
81	Thallium .	204.39	205, 203	207, 208, 210
82	Lead .	207.21	208, 206, 207, 204 (203, 205, 209)	210, 211, 212, 214
83	Bismuth .	209.00	209	210, 211, 212, 214
84	Polonium .	210.00		210, 211, 212, 214, 215, 216, 218
85	—	—	—	—
86	Emanation (Radon) .	222		222, 219, 230
87	Eka-caesium .	?		
88	Radium .	226.05		226, 223, 224, 228
89	Actinium .	?		227, 228
90	Thorium .	232.12	232	232, 227, 228, 230, 234
91	Proto-actinium .	?		231, 234
92	Uranium .	238.07		238, 235, 234

40. **The Whole-Number Rule, and Deviations from it.**—Attention has already been called to the fact that the masses of isotopes are all very nearly whole numbers, and that therefore Prout's hypothesis is more nearly true than was believed during the last century. This fact, of course, is what would be expected when it is realised that the electron has an extremely small mass, and that even 92 of them, the maximum number of extra-nuclear electrons found in any element occurring naturally, will weigh only a small fraction of a unit.

It is, however, true that there is usually a very slight deviation from the rule that the mass of an isotope is a whole number. This difference varies from nucleus to nucleus and is sometimes positive, but more often negative. To express it, Aston introduced the term *packing fraction*, which is defined as

$$\frac{\text{isotopic atomic weight} - \text{mass number}}{\text{mass number}} \times 10^4$$

As we have seen, nuclei are made up of protons and neutrons. Both the proton and the neutron have masses slightly greater than 1, but, except for the lighter nuclei the mass of the isotope is slightly less than the mass number. Hence, in these cases, when the protons and neutrons come together to form nuclei some of their mass disappears. It must be converted into energy. The amount of mass converted into energy varies with the way in which the protons and neutrons are packed in the nucleus—hence the term *packing fraction*.

It is a general principle that the less energy a system contains the more stable it is. Hence it would be expected that nuclei with negative packing fractions would be stable, and those with positive ones would be unstable. Although this is not completely true, other factors entering into the question, the packing fraction certainly has some bearing on the stability of nuclei.

A curious alternation in the packing fraction is noted with the lighter elements (atomic numbers 10–31) as we pass from elements of odd atomic number to their neighbours with even atomic numbers, the elements of odd atomic number having a higher packing fraction than the adjacent elements. This would imply an alternation of stability. There are several other properties of elements which alternate in the same way.

It is entirely because of the fact that nuclei have different packing fractions that it is possible, by changing one nucleus into another, to set free vast amounts of energy (§ 47).

41. **The Physical Determination of Atomic Weights.**—If we knew the packing-fractions of the different elements and the proportions of the isotopes occurring in the element as commonly prepared, it would be possible to calculate the atomic weight.

TABLE XI.—PACKING-FRACTIONS OF ATOMS

Atom.	Packing-fraction $\times 10^4$.	Atom.	Packing-fraction $\times 10^4$.
H	77.8 ± 1.5	As	-8.8 ± 1.5
He	5.4 ± 1	^{52}Cr	-10 ± 3
^6Li	20.0 ± 3	^{78}Kr	-9.4 ± 2
^7Li	17.0 ± 3	^{79}Br	-9.0 ± 1.5
^{10}B	13.5 ± 1.5	^{80}Kr	-9.1 ± 2
^{11}B	10.0 ± 1.5	^{81}Br	-8.6 ± 1.5
C	3.0 ± 1	^{82}Kr	-8.8 ± 1.5
N	5.7 ± 2	^{83}Kr	-8.7 ± 1.5
O	0.0	^{84}Kr	-8.5 ± 1.5
F	0.0 ± 1	^{86}Kr	-8.2 ± 1.5
^{20}Ne	0.2 ± 1	^{98}Mo	$ca - 5.5$
^{22}Ne	$ca 2.2$	^{100}Mo	$ca - 5.5$
P	-5.6 ± 1.5	I	-5.3 ± 2
^{35}Cl	-4.8 ± 1.5	^{120}Sn	-7.3 ± 2
^{36}A	-6.6 ± 1.5	Cs	-5 ± 2
		^{134}Xe	-5.3 ± 2
^{37}Cl	-5.0 ± 1.5	Ba	-6.1
^{40}A	-7.2 ± 1	^{200}Hg	$+0.8 \pm 2$
		Tl	$+1.8$
		^{206}Pb	$+0.8 \pm 2$

This had been attempted almost as soon as the existence of isotopes of the common elements had been proved. The relative abundance of the isotopes was estimated visually from the photographs obtained by the first mass-spectrograph. At first the results were found to be in excellent agreement with the chemical values; but when krypton was studied, the first serious discrepancy arose. With this element six lines were found, each of them corresponding to an integral mass, and therefore belonging to a definite isotope. The position of the centre of gravity of this group was estimated, and gave an atomic weight for the element of 83.5 ± 0.3 . The international figure, based on determinations of the density, was 82.92. With boron, two isotopes were found of masses 10 and 11, and the atomic weight calculated from these was less than the chemical value of 10.90. Xenon gave a mean value of 131.3 ± 0.3 , whereas the international value was 130.2. The greatest discrepancy of all was with antimony, the isotopes of which were 121 and 123, whereas the inter-

national atomic weight was lower than either, viz., 120.2. Beryllium, according to positive ray analysis was a simple element, and hence its atomic weight should be integral. The value accepted was 9.1, which was considered to be too far removed from an integer. The fact that the physical values differed from the chemical in these cases led to a redetermination of these atomic weights by chemical methods, and in the cases of boron, beryllium and antimony, the discrepancies were reduced to very small magnitudes, although they remained for krypton and xenon.

The first actual determinations of the relative abundance of isotopes in a given element, apart from the somewhat rough visual determination, were carried out by Dempster, who analysed the positive rays magnetically, and compared the currents caused by the rays due to the various isotopes, when they ionised a gas. The method has already been described (§ 39). The masses of the isotopes were not determined, but by assuming that the whole number rule was valid, he was able to show that the atomic weights of potassium, magnesium, calcium and zinc were in fair agreement with those derived chemically.

In 1925, Aston devised the second mass-spectrograph, which has already been described, and with its aid he was able to show that the whole number rule was not strictly valid owing to the existence of "packing-fractions".

When these are known the correct mass of any isotope can be written down, and this is, of course, a preliminary to any calculation of atomic weights by the physical method. It was still necessary, however, to devise some more accurate method of comparing the relative abundance of the isotopes in any given element, and this was done by Aston, who invented a photometric method of estimating the intensity of the blackening on the photographic plate upon which the isotopic lines were registered.

At first krypton was taken as the standard element, as it has six isotopes, and provides rays in which it is safe to assume that the proportion of the isotopes does not vary. The relative abundance of the isotopes of mass 84 and 86 respectively was first determined by the method of intermittent exposures. By a special mechanical arrangement the lines were photographed with normal and with reduced times of exposure, the two images being separated from each other by slightly varying the electric field. The effect of this change of field was eliminated by taking the next picture with the field change reversed. By breaking up the exposure into small ones the continuous change in the intensity of the source was compensated for as far as possible. The ratio of the exposures was altered until the stronger of the two lines and the normal one of the weaker were virtually equal. The ratio for correct equality was calculated, and when corrected for the effect of the penumbra of the neighbouring lines and for the relative positions of the two lines on the

plate, the value 3.41 was obtained for the ratio of the abundance of ^{84}Kr , compared with that of ^{86}Kr . The process was repeated for the other isotopes, and the following figures were obtained for the percentage abundance of the isotopes:—

78	80	82	83	84	86
0.42	2.45	11.79	11.79	56.85	16.70

These give a "mean mass number" of 83.857, which, when corrected, for a packing-fraction of -8.8 in 10,000 gives the atomic weight ($O = 16$) as 83.783. This was considerably higher than the chemical value (82.92) then accepted. Allen and Moore (*J. Amer. Chem. Soc.*, 1931, **53**, 2512) then redetermined the density of krypton from liquid air residues, and found the value 83.6 for the atomic weight, which is in agreement with Aston's figure. The international value now accepted is 83.7.

TABLE XII.—CHEMICAL AND PHYSICAL ATOMIC WEIGHTS

Element.	Atomic Number.	International Atomic Weight.	Physical Atomic Weight.	Element.	Atomic Number.	International Atomic Weight.	Physical Atomic Weight.
H	1	1.0078	1.00761	Sr	38	87.63	87.64
He	2	4.002	4.00136	Nb	41	93.3	92.90
Li	3	6.940	6.928	Mo	42	96.0	95.97
B	5	10.82	10.803	Ru	44	101.7	(101.1)
C	6	12.00	12.0037	Sn	50	118.70	118.71
N	7	14.008	14.008	Sb	51	121.76	121.78
O	8	16.000	16.000	Te	52	127.61	127.58
F	9	19.00	18.996	I	53	126.932	126.91
P	15	31.02	30.98	Xe	54	131.3	131.26
Sc	21	45.10	44.96	Cs	55	132.91	132.91
Cr	24	52.01	52.01	Ba	56	137.36	137.43
Zn	30	65.38	65.33	Ta	73	181.4	180.89
Ge	32	72.60	72.65	W	74	184.0	183.96
As	33	74.91	74.92	Re	75	186.31	186.22
Se	34	78.96	78.96	Os	76	191.5	190.31
Br	35	79.916	79.911	Hg	80	200.61	200.62
Kr	36	83.7	83.767	Tl	81	204.39	204.41
Rb	37	85.44	85.43	Pb	82	207.22	207.19

(From the *Journal of the Chemical Society*, 1932, 2893; with some corrections from more recent work.)

The atomic weights of the other elements were more difficult to determine, as the apparatus would not resolve the lines sufficiently to enable one of the lines to be photographed between two others without overlapping. In this case, a large number of short exposures of different times was used, and the best mean values adopted from the curves obtained.

The atomic weights of a large number of elements have now been determined by this physical method, and some of the results are given in Table XII.

Where the values differed from those accepted and determined on the chemical basis, re-determination on this basis has usually shown that the physical method gave the correct result. The atomic weight of selenium, which differed from the chemical value by 0.24 unit, was re-determined chemically by Hönigschmid, who found a value close to that obtained physically.

42. The Separation of Isotopes.—The separation of isotopes is a matter of extraordinary difficulty. Nevertheless the work leading to nuclear fission and the utilisation of atomic energy depended upon the large scale separation of isotopes, and great strides have been made towards the solution of the problem, especially in specific cases.

Physical methods are commonly used. The first method that would appear to be possible would be to use a positive-ray apparatus, for, as we have already seen, this separates the isotopes completely. Oliphant, Shire, and Crowther (1934) obtained very small amounts (rather less than one ten-millionth of a gram) of the isotopes of lithium of mass number 6 and 7 by this method. The apparatus has since been much improved and the method has been used to separate the isotopes of uranium on a large scale in connection with nuclear fission.

Where there are differences in density, it should be possible to separate isotopes by the process of diffusion. This has been tried with hydrogen chloride, but the process is very tedious, since the difference in density is so small. Harkins, who attempted to separate hydrogen chloride into two fractions, employed 20,000 litres of the gas, and obtained finally a difference of molecular weight of 0.055 unit. Aston, somewhat earlier, had attempted to separate neon into fractions by the same method, and finally obtained two fractions having densities 20.15 and 20.28 respectively, the normal density being 20.20. The neon isotope of mass 22 has now been separated perfectly from the isotope of mass 20 by a diffusion process.

The fact that the rate of evaporation of a mixture of atoms varies with the mass of the atom has also been used for their separation. A greater number of the light atoms will escape from the surface in a given time, and the residue will therefore be richer in the heavier atoms. The

rates of evaporation of otherwise identical atoms under the same conditions are inversely proportional to the square root of their masses. By keeping the pressure on the surface of the liquid low, none of the atoms escaping will return to the surface, and so a partial separation can be effected.

The method has been used by Brönsted and Hevesy in the separation of mercury into two fractions, one containing a greater proportion of the lighter isotopes, and one containing a greater proportion of the heavier. The mercury was allowed to evaporate in a high vacuum, at a temperature of 40° – 60° C., and was condensed on a surface 1–2 cm. away, cooled in liquid air. Actually, the mercury was placed in the space between the two walls of a Dewar flask containing liquid air. The lighter atoms which evaporated off first were condensed to the solid state on the cold surface, and therefore had no chance of returning to the liquid. After the evaporation had gone on for some time, the mercury residue was removed, and the solid distillate was melted, and kept apart. The process was repeated with this, and so on. If the density of ordinary mercury is taken as 1, the densities of the lightest and heaviest fractions were 0.99974 and 1.00023 respectively.

Harkins improved the apparatus, and by working on a larger scale was able to obtain mercury having an atomic weight differing by 0.189 unit from that of ordinary mercury. The experiment has also been repeated by Hönigschmid and Birkenbach, who obtained fractions of atomic weights 200.564 and 200.632 respectively, whereas the atomic weight of ordinary mercury is 200.61.

The method has also been applied to potassium by Hevesy, and to zinc by Egerton.

The fractionation of isotopes by electrolysis is a method that has been used, particularly in the separation of the hydrogen isotopes. Kendall (1933) claims to have effected a slight separation of mercury isotopes by this method. Electrolysis of an acid solution of mercurous nitrate, using a low voltage, and low current density, gave mercury with a density 0.999981 that of ordinary mercury.

The method of thermal diffusion has been applied very successfully to the separation of isotopes by Clusius and Dickel (1938). It is based primarily on an observation by Enskog (1911), who showed that if a gaseous mixture of molecules of different mass was enclosed in a tube which was hotter at one end than at the other, the heavier molecules would tend to diffuse towards the cooler end. This process of thermal diffusion would go on until it was balanced by the effect of ordinary diffusion, which would, of course, work in the opposite direction.

Whilst this process may bring about a reasonable separation of gases which differ considerably in mass and nature, without modification it is of very little use for the separation of isotopes which do not differ much

in mass. In the method devised by Enskog, and used by Chapman and Dootson for the separation of a mixture of hydrogen and carbon dioxide, convection currents are avoided by having the hot plate parallel to, and above, the cold one. If, however, the parallel plates are placed vertically convection currents may be made to enhance the separation. In the diagram convection currents occur as shown by the arrows. At the same time thermal diffusion brings about a concentration gradient with the lighter component near the hot plate. This gas reaching A is carried upwards, that at B travels downwards. This means that the lighter fraction will become concentrated at the top of the apparatus and the heavier at the bottom. In the apparatus used by Clusius and Dickel for this purpose, a vertical glass tube was used with an electrically heated wire running down the centre. The glass tube was cooled on the outside by a current of cold water. With apparatus of this kind, the tube being 36 metres long, the isotopes of chlorine have been separated almost completely.

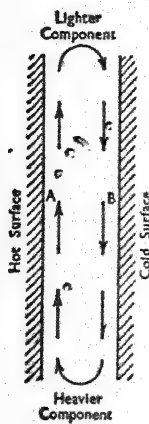


Fig. 36.

The method has been used to obtain the uranium isotope of mass 235 for nuclear chain reactions in uranium (§ 49). In this case uranium hexafluoride, UF_6 , was used as the carrier gas.

The method of thermal diffusion can also be applied to liquids, but is limited to substances which are not decomposed at the temperature of the hot wire.

Although the chemical reactions of isotopes of an element are very similar, the rates of these reactions differ when the different isotopes are used, and this fact can be employed to effect a partial separation of isotopes. We may consider the simple reversible exchange reaction between the light isotope of hydrogen $^1\text{H}_2$, or simply H_2 , and heavy water, $^2\text{H}_2\text{O}$, or D_2O (the symbol D stands for the heavy isotope of hydrogen which is called deuterium):



It is found that if ordinary hydrogen is slowly bubbled through heavy water, so that equilibrium is attained, the gaseous product contains an increased proportion of deuterium. In the absence of a catalyst however, the attainment of equilibrium is so slow that the reaction is of no practical use.

A similar reaction occurs between oxygen and water:



but a relatively high temperature and a catalyst are normally required

if the reaction is to proceed at a reasonable rate. The proportion of $^{18}\text{O}_2$ in atmospheric oxygen is greater than in water and it is thought by some that the above reaction is responsible for this.

The difference in rate of reaction of isotopes is due mainly to differences in zero-point energy, *i.e.*, the energy which a molecule still possesses even at the absolute zero of temperature. This depends on the mass of the molecule. Other factors influencing the equilibrium constant of an exchange reaction are the molecular weights and moments of inertia of the molecules which are again, of course, determined by the masses of the component atoms.

43. The Hydrogen Isotope, ^2H , or Deuterium, D.—The fact that the physical atomic weight of hydrogen differed from the chemical value, though by very little (the physical atomic weight is 1.00756, whilst the chemical value is 1.0078, both calculated on the chemical standard) led Birge and Menzel in 1931, to suggest that ordinary hydrogen consists of a mixture of the atoms of mass 1 (approx.), and a very small amount of an isotope of double this mass, only the former having been observed in Aston's experiments fixing the physical atomic weight. The more recent work has shown that the difference between the two atomic weights can be approximately accounted for by the proportion of the isotope present, the ratio of the abundance of ^1H to that of ^2H being 6,500 to 1.

The residues left after the evaporation of large quantities of liquid hydrogen were found to give faint lines corresponding to ^2H , when examined spectroscopically (Urey, Brickwedde and Murphy, 1932). In 1932 Bainbridge also demonstrated the existence of the isotope by means of the mass-spectrograph, obtaining a value for its mass of 2.01351 ± 0.00018 , referred to $^{16}\text{O} = 16$. The nucleus of the heavy isotope of hydrogen is sometimes called the deuteron. It consists of one neutron and one proton.

The separation of the hydrogen isotope was carried out by Washburn and Urey, in 1932, by the examination of water from commercial electrolytic cells which had been working for some years. There was shown to be more ^2H in this water than in ordinary water. Lewis and Macdonald electrolysed 20 litres of water from an old electrolytic cell, which contained alkali, with a current of 250 ampères, until the volume was only 10 per cent. of the original. One-tenth was neutralised with carbon dioxide and the rest distilled. Then the two sets were combined. The process was repeated until only 0.5 c.c. was left. The water they finally prepared had a specific gravity of 1.073, and probably contained 65 per cent. of heavy water, $^2\text{H}_2\text{O}$.

If water is distilled through a long fractionating column, quite a large separation of isotopes results, especially if the work is carried out under reduced pressure. Practically pure "heavy water" was obtained by

Lewis and Macdonald, who found that its freezing point was $+3.8^{\circ}\text{C}$., and boiling point 101.42°C . Many other physical properties of the water have been examined. It has a maximum density at 11.6°C .

The hydrogen isotope, ^2H , itself has been prepared in a state of purity by Hertz, Schutze, and Harmsen, by a process of diffusion. Since the two isotopes differ in mass by approximately 100 per cent., their separation by this method should be much more easy than for other elements. Water from an electrolysis apparatus was reduced by magnesium. The hydrogen thus obtained consisted of $^1\text{H}_2$, and composite molecules, made up of an atom of each isotope, $^1\text{H}^2\text{H}$, with only a small amount of ^2H . By passing the electric discharge through the mixture, the composite molecules were broken down into their atoms, which recombined to form molecules of $^1\text{H}_2$ and $^2\text{H}_2$. The mixture now contained only the two molecular species, and was readily separated into the two constituents by diffusion. In this way the ^2H isotope was obtained spectroscopically pure.

In most cases, the chemical properties of isotopes are very nearly the same, and this also applies to compounds made from different isotopes. In the case of hydrogen, however, this does not appear to be so, for the compounds made from one isotope are different in some important respects from those made from the other. Thus, "heavy water", which is $^2\text{H}_2\text{O}$, is toxic to certain forms of life, a fact which had been predicted by Lewis even before the water was obtained.

Because of the considerable difference in zero-point energy of H_2 , HD , and D_2 they react with other elements at different rates. It has been reported that electrolytic hydrogen is more active in the Haber ammonia synthesis than other hydrogen prepared from steam, the velocity of reaction being 10–40 per cent. greater. This is probably due to the fact that when water is electrolysed the heavy isotope is left in the water in the cell, whilst the lighter one is evolved.

It is a matter of some importance to note what effect the discovery of this isotope has on the determination of the composition of substances containing hydrogen. In determining the composition of water, or of ammonia, or any other gas containing hydrogen, it is necessary to make certain that the "pure" gas is used, or else its composition must be known. The source of the hydrogen used in the experiments must be stated. This difference in composition of hydrogen obtained from different sources explains the differences that have been found in the composition of water (§ 13).

It is clearly advantageous to retain the oxygen standard for atomic weight determinations in the light of the new discovery. As has been stated already (§ 11), the determination of the atomic weight of a solid element usually involves the determination of the equivalent. This is often found from the weight of the element that will combine with 8 gms.

of oxygen. If, however, the scale $H = 1$ is taken, the equivalent of oxygen is no longer 8, and moreover its determination will not be a simple matter, since it depends on the composition of water.

With the existence of the two isotopes of carbon, ^{12}C and ^{13}C , and the two isotopes of hydrogen, the properties of which are different from each other, a new organic chemistry is possible, in which the compounds are made by combination of the various pure isotopes. The use of heavy water in medicine may also prove a useful field of research. A preparation containing 30 per cent. $^2\text{H}_2\text{O}$ is now a commercial article.

Heavy water has proved to be of importance in the controlled chain-fission of uranium (§ 50).

44. Variation of the Atomic Weight of an Element with its Source.—

It is a curious fact that no matter how an element is prepared chemically in the laboratory, the proportion of the isotopes present in it is always the same. This may not be so, however, with naturally occurring elements and compounds. Some of these may have been formed from radioactive sources, and they have different atomic weights according to the source from which they are derived. This is known to be the case with lead. Lead minerals derived from different radioactive sources have different atomic weights. Thus the atomic weight of lead from a deposit supposed to have come from uranium was 206.08, a mixed Australian mineral gave an atomic weight 206.34, whilst ordinary lead has the atomic weight 207.19.

The atomic weight of calcium is found to differ according to its source. A. V. Frost and O. Frost claim to have found a concentration of ^{44}Ca in a specimen of potash felspar, the value 40.23 being obtained for the atomic weight of the calcium in this mineral, whereas that of ordinary calcium is 40.08.¹

The atomic weight of three specimens of boron from different sources gave the values 10.847, 10.823 and 10.818. The differences are too great to be ascribed to experimental error. As boron is light, its isotopes differ in mass by 10 per cent., and consequently the effect is more marked with this element than with others.

The variation in atomic weight of hydrogen according to its source has already been mentioned (§ 43).

45. Atomic Transmutation.—

The radioactive elements are continually undergoing spontaneous disintegration, and new elements are being formed. This process is going on continuously, and no method of stopping, or of accelerating it is known. Thus, transmutation is occurring, but we have no control over it.

¹ The Ca of atomic weight 40.23 is supposed to have been formed from K^{41} by a β -ray change. The existence of Ca of high atomic weight in minerals has been confirmed by Kendall, Smith, and Tait.

It is to the transmutation of ordinary elements that attention is called by recent research. The properties of an element depend on the atomic number, which is numerically identical with the resultant positive charge on the nucleus. To transmute an element, the nucleus must be altered artificially, *i.e.*, the process which goes on naturally with the radioactive elements must be carried out in the laboratory. Practically all the mass of the atom is concentrated in the nucleus, and consequently almost all the energy. If any change is to be brought about in the nucleus, energy of a similar amount and concentration must be supplied.

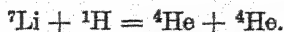
α -particles from radioactive bodies are fairly heavy, and although their speeds do not approach those of β -particles, they are possessed of a fairly great amount of energy. According to the Einstein theory of relativity, the mass of a moving charged body depends upon its velocity, becoming infinite when the velocity is that of light (§ 22). The more rapidly the α -particle moves the greater is its kinetic energy ($\frac{1}{2}mv^2$, where m is the mass, and v the velocity), not only because the velocity increases, but because, in consequence of the latter, the mass also increases. The more rapidly moving α -particles will therefore be possessed of high energy.

Rutherford, in 1919, found that when α -particles of range 7 cm. from Ra-B and Ra-C were fired into nitrogen, a certain amount of transmutation took place. The tracks of the particles were made evident by means of scintillations and by the Wilson cloud-chamber (§ 21), and evidence was found of the formation of high-speed hydrogen nuclei or protons. It must be remembered that the amount of transmutation was exceedingly small, and would never have been observed unless extraordinarily sensitive methods had been used for detecting it. Other elements were found to be disintegrated in the same way. Boron, nitrogen, fluorine, sodium, aluminium, phosphorus, neon, magnesium, silicon, sulphur, chlorine, argon and potassium, all gave a small number of charged hydrogen nuclei on bombardment with swift α -particles.

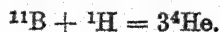
It has been pointed out that in order to obtain transmutation, particles possessing high energy are required. These need not be α -particles; protons will also serve the purpose. Attempts to use protons, however, from sources such as discharge tubes, were not at first successful, owing to the fact that it seemed to be necessary to employ very high potentials in the discharge tubes to obtain protons with the requisite energy. These difficulties were entirely overcome by the adoption of a device for enhancing the energy of the protons. As early as 1902, Wien had shown that protons could be accelerated as they passed through a perforated cathode. After passing through the "canal", they were passed into a highly evacuated space, and then accelerated by means of an electric field of great intensity.

This method of obtaining rapid protons was used with success by

Cockcroft and Walton. By passing the protons from a discharge tube through a field of 125,000 volts in an evacuated space they were speeded up to such an extent that they possessed velocities comparable with those of the α -particles from polonium. Bombardment with these high-speed protons was applied to the disintegration of lithium. A large number of α -particles was emitted. The change appears to be that the nucleus of lithium, of mass 7, and atomic number 3, which contains 3 protons and 4 neutrons, takes up one proton, and then splits into two α -particles of mass 4 and charge 2:—



Boron is quite easily broken down by protons, with the emission of α -particles. The boron nucleus of mass 11, and containing five protons, takes up a proton of mass 1, and breaks down into three α -particles:—



Another method of producing rapid protons for these experiments has been devised by Lawrence in America, and by Gerthsen in Germany. They have accelerated the particles by making them pass through the same potential over and over again. The process is known as "multiple acceleration", and is carried out in a cyclotron. In this way they have been able to produce protons of energy 1.5 million volts, by using an accelerating potential of only 10,000 volts. Oliphant and Rutherford devised a special accelerating tube which will produce a narrow and intense stream of protons with voltages up to 200 kilovolts.

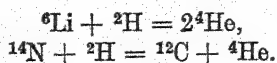
Other types of apparatus used for the production of high-speed particles are the betatron and the synchrotron.

Hard γ -rays are also possessed of sufficient energy to bring about disintegration. It will be shown in the next chapter that the energy associated with a radiation of frequency ν , is proportional to the frequency. Thus, the smaller the wavelength, the greater the frequency, and the greater the energy.

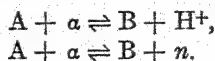
Neutrons are particularly valuable as bombarding particles for bringing about atomic transmutation because they are uncharged. Charged particles are slowed down considerably in passing through matter because of the other charged particles (electrons and protons) with which they interact. A neutron, however, goes straight on until it encounters a nucleus head-on; if it is then captured an unstable nucleus may result, when an artificially radioactive nucleus will have been formed. On the other hand if the nucleus is stable, the original element will have been changed to another.

Experiments on atomic transmutation have been carried out, using the nucleus of the hydrogen isotope, ${}^2\text{H}$, or deuteron, as the firing

particle. It is possible in this way to transform lithium into helium, and nitrogen into carbon.



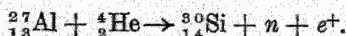
Summing up, the artificial disintegration of the elements can be brought about by bombardment of the atom with protons, deuterons, α -particles and neutrons. The processes are reversible and take place according to the general equations



or

There is thus in the nucleus an exchange of a helium nucleus with a proton, or with a neutron. The first of these reactions may be written $A(\alpha p)B$: this means that A is bombarded with α -particles, which leads to the production of B and protons. The reaction is called an αp reaction. Similarly the second reaction may be written $A(\alpha n)B$ and is called an αn reaction.

In all these processes, the disintegration apparently stops when the bombarding particles are switched off, but Curie and Joliot discovered an artificial radioactivity when certain elements are disintegrated. The radioactive elements themselves possess unstable nuclei, and the latter break down according to an exponential law. When aluminium is bombarded with polonium α -particles, the final product is the silicon nucleus of mass 30 and charge 14, together with neutrons and positive electrons:—

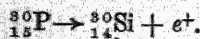


The top figures indicate masses, the lower ones charges.

When the bombarding α -particles are removed, evidence of the emission of positive electrons can still be obtained. Meitner photographed them nine minutes after the bombarding particles had been switched off, using the cloud-chamber method. There is evidence that the primary change in this disintegration is

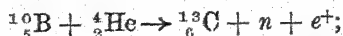


The ${}^{30}\text{P}$ nucleus is unstable, and breaks down like the nucleus of a radioactive atom, according to the equation

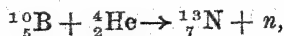


This change occurs even when there is no bombardment taking place; it is an artificial radioactive change, and follows the exponential law for decay.

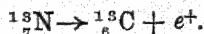
Similarly Meitner has photographed the emission of positive electrons from boron twelve minutes after exposure to polonium α -particles. The total change here is



but the primary change is doubtless



with the radioactive disintegration of the unstable nitrogen nucleus according to the equation



Fermi has shown that slow neutrons can react with almost all nuclei, giving, in most cases, radioactive products. Bombardment with slow neutrons can lead to four types of reactions (na), (np), ($n\gamma$) and ($n2n$). The products of the first three types of reactions are radioactive and emit negative electrons; those of the ($n2n$) reaction can emit either positive or negative electrons. The ($n\gamma$) is the most common of these reactions.

A very large number of nuclear reactions have now been studied, and it is impossible in a general text-book to mention any of them in detail. A list of nuclear reactions giving rise to artificial radioactivity which have been investigated will be found in the specialist text-books, such as those named at the end of this chapter.

46. The Detection of Atomic Transmutation.—In the early work on atomic transmutation the amounts of the products were so small as to be unweighable and even too minute to respond to chemical tests. Although a few elements have now been obtained by this method in quantities large enough to admit of chemical identification, and even to enable their properties to be studied, the majority of the products are identified by physical methods.

Fast-moving charged particles are capable of ionising molecules of gases. This ionisation can be detected in a number of ways. One method is by means of the Wilson cloud-chamber already described (§ 26). This is very largely used because not only does it enable the existence of particles to be detected, but a quantitative estimate of their mass can be obtained from the length of the tracks.

Other apparatus for detecting and measuring ionisation are the various types of "counter". The Geiger-Müller counter consists essentially of a wire surrounded by a tubular electrode in an ionisation chamber. When fast-moving ionising particles enter the chamber they produce primary ions in the gas in the chamber. If the potential difference between the wire and the electrode is sufficiently great, the primary ions produce a large number of secondary ions, and a discharge

is initiated in the gas. This means that a current flows between the electrodes, and can be detected in the usual way. The current would, however, continue indefinitely once the discharge was started, and some method has to be adopted to "quench" it. There are various ways of doing this which need not be entered into here.

A modification of the Geiger-Müller counter is the proportional counter which is so arranged that the total number of ions produced is proportional to the number of primary ions formed. It is possible with this apparatus to distinguish between ionisation produced by different types of particles.

Neutrons, of course, cannot be detected directly by means of ionisation, as, being uncharged, they are unable to produce ionisation in a gas. However, the ionisation method can still be used indirectly. The neutrons are made to bombard atoms, usually boron, which leads to the production of lithium nuclei and alpha particles. These have sufficient energy to bring about ionisation in an ionisation chamber or counter.

Another method of measuring neutron densities is to use the neutrons to produce artificially radioactive nuclei and then measure the degree of activity of the product.

47. Energy Considerations.—It has already been stated that the particles making up the nucleus of elements may be packed in different ways so that the total mass is not necessarily the sum of the masses of the constituent protons and neutrons. It has also been stated that there is no law of conservation of mass, but a law of conservation of mass and energy taken together. If, then, the nucleus of an atom could be made up from its constituent parts, and its total mass were less than the sum of the masses of these parts, the difference would be radiated as energy. It has not been possible to build up nuclei in this way, but it has been possible, by the methods outlined above, to change nuclei into others. In these cases it might well happen that the sum of the masses of the interacting particles was greater than the sum of the masses of the products, in which case energy would be made available.

To take a simple example. The bombardment of lithium with energetic protons gives rise to helium nuclei, the reaction being



The mass of ${}^7_3\text{Li}$ is 7.01818, of ${}^1_1\text{H}$ 1.00813, and of ${}^4_2\text{He}$ 4.00389. The total mass on the left-hand side is thus 8.02631 units, and on the right 8.00778 units. Hence 0.01853 units of mass have disappeared and will be transformed into energy.

If we deal in grams 0.01853 gm. of mass disappear for every 8.00778

gm. of helium produced. To find out the energy corresponding to this loss of mass we use the Einstein energy relation

$$E = mc^2$$

where E is the energy, m is the mass, and c is the velocity of light. Substituting 0.01853 gm. for m and 3×10^{10} cm. per sec. for c

$$\begin{aligned} E &= 0.01853 \times 9 \times 10^{20} \text{ ergs} \\ &= 0.16677 \times 10^{20} \text{ ergs} = 4.63 \times 10^5 \text{ kilowatt hours.} \end{aligned}$$

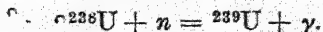
Thus, a very considerable amount of energy is set free. It is, of course, attached to the helium atoms formed, which move away with this energy. This has been verified experimentally, and is a strong confirmation of the truth of the Einstein relation.

The question arises as to whether this energy is economically worth tapping, and, if so, how it can be utilised. In the case of a simple nuclear reaction like that quoted above, considerable energy has to be used to impart sufficient energy to the protons to enable them to penetrate the lithium nucleus and interact with it. Even then, very few of the accelerated protons actually collide with lithium nuclei. There is thus a considerable waste of energy, and it would actually be unprofitable to utilise reactions similar to the above for the production of atomic energy.

As has been mentioned, neutrons are more effective than other particles in bringing about nuclear reactions, and it might be expected that better results would be obtained in this case. The trouble here is that neutrons are difficult to produce. They may be obtained by the action of α -particles from radium on beryllium, but radium is very expensive; they can also be produced by bombarding light elements with ion beams. In this case we have the same difficulty as before, namely, that few ions are effective in producing neutrons, and the process would use up more energy than it produced.

The whole difficulty has been overcome by the discovery of a nuclear reaction in which neutrons are actually produced. These are able to transform neighbouring nuclei when more neutrons are emitted. Such a reaction is called a chain reaction, and once started proceeds spontaneously.

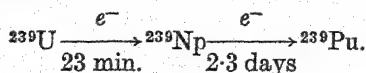
48. New Elements.—When uranium is bombarded with neutrons two processes can take place, neutron capture, and nuclear fission. Neutron capture occurs when a nucleus of the uranium isotope of mass 238 captures slow neutrons giving uranium 239:



This is an example of a (n, γ) reaction.

Uranium 239 is radioactive and emits β -particles giving an element of atomic number 93. This element, called neptunium, Np, does not occur in nature. Neptunium decays with β -particle emission to

element 94, plutonium, Pu. The half-lives of ^{239}U and Np are 23 minutes and 2.3 days, respectively. Plutonium is also radioactive. It emits α -particles and has a half-life of 24,000 years. Thus, the result of neutron capture is that the ^{238}U is converted to plutonium, which is comparatively stable.



In addition to elements 93 and 94, elements 95 (americium, Am), 96 (curium, Cm), 97 (berkelium, Bk), and 98 (californium, Cf) have also been prepared artificially.¹ The elements 90 to 98 are thought to form a part of a second rare-earth series called the actinides (the first rare-earth series called the lanthanides starts with the element after lanthanum). Some think, however, that the second rare-earth series begins with uranium.

Nuclear reactions have not only produced elements of higher atomic number than uranium, but have also been responsible for filling in the gaps of the periodic table at elements 43, 61, 85, and 87.

49. Nuclear Fission.—As previously stated uranium can also undergo fission. In this process the nucleus splits mainly into two large fragments and two or three neutrons. Fission occurs when ^{238}U or ^{235}U is bombarded with fast neutrons, or better when ^{235}U is bombarded with slow neutrons. A number of nuclei have been identified as the two larger fission fragments. They range from zinc, of mass number 70, to europium, of mass number 160. Barium and krypton and the nuclei close to these elements are the chief products. The products are all radioactive and go through a number of β -decays before reaching stability. The series of decays may involve up to six stages.

The mass of the fission products is less than that of the original nucleus. Hence a large amount of energy corresponding to this loss of mass is released in each fission. The average energy released per fission is 200×10^6 electron-volts. The neutrons emitted during a fission can then bring about further fissions and thus lead to a rapidly propagating chain reaction, which is accompanied by the release of a large quantity of energy. Plutonium is also fissile. The chain reaction produced by the fission of ^{235}U or ^{239}Pu is utilised in the atomic bomb.

50. Nuclear Reactors.—Nuclear reactors are used for the production of plutonium on the large scale. The reactor pile is a structure consisting of cylindrical lumps of uranium arranged in a lattice of graphite rods. The pile is surrounded by concrete to protect personnel working on it from the effects of radiation. The action of the pile is started by exposing it to a source of neutrons. Fission of ^{235}U is effected by the action of both fast and slow neutrons with further

¹ The preparation of elements 99 and 100 has recently been announced.

production of fast neutrons. Fast neutrons also cause the fission of ^{235}U nuclei. The fast neutrons are slowed by the graphite rods¹ and become slow neutrons. These can be captured by the ^{238}U nuclei leading to the production of plutonium, which, as has been said, is also fissile. When a pile is operating steadily one neutron of each fission should be available to give a further fission, so as to keep the pile operating. The remaining neutrons are available for the production of plutonium. The pile is therefore a controlled chain reaction. If a pile appears to be getting out of control, cadmium rods can be lowered into it. Cadmium captures neutrons very easily, and the result is that the neutron flux in the pile can be regulated. Nuclear reactions involving either fast or slow neutrons can be carried out by placing the substance to be bombarded in the fast or slow neutron portion of the pile. The energy produced in the pile is likely to become an important source of power.

51. The Positive Electron, or Positron.—Besides the neutron, another particle, the positive electron, has been discovered. During the study of cosmic radiation by the cloud-chamber method, some of the particles were found to be deflected in an opposite direction from that suffered by the negative electrons, when a magnetic field was applied (Anderson, 1932; Blackett and Occhialini, 1933). The particles must therefore bear a positive charge. They can also be produced by the bombardment of matter by hard γ -rays, and by neutrons. The charge and the mass of the particle have been obtained from a study of the ionisation that it produces when passing through a gas. Anderson has shown that the difference in ionising powers of fast positive and negative electrons is certainly less than 20 per cent. The mass of the positive electron has been deduced by Blackett to be 1.04 ± 0.14 , if the mass of the negative electron is taken as 1.

It is obvious, then, that we are here dealing with a positive particle smaller than the proton, yet bearing the charge of the proton. It has been customary to regard the proton as the elementary positive charge, but it seems likely that this place is taken by the positive electron.

The positive electron cannot exist for long far outside the nucleus, and it is extremely probable that its expulsion is accompanied by the simultaneous expulsion of a negative electron.

52. The Neutrino.—Considerations of the angular momentum of the nucleus lead to the conclusion that if the laws of conservation of energy and of momentum are to hold, the existence of a new particle, called the neutrino, must be postulated. It is very light, at least as light as the electron, and has no charge. Fermi, indeed, ascribes to it a zero rest-mass.

Experiments to detect the neutrino directly have so far failed. This is not surprising in view of its exceedingly small mass and lack of charge. It is claimed, however, that experiments on the recoil of atoms emitting β -rays, indicate its existence (Allen, 1942). Chadwick and Lee showed that if the neutrino does exist it produces less than one pair of ions in traversing 150 km. of air at N.T.P.

53. Cosmic Radiation.—The earth's atmosphere is bombarded by a positively charged corpuscular radiation which is said to be cosmic because it comes from outside the earth. The particles present in the radiation before it strikes the atmosphere are mainly protons and the nuclei of

¹ The graphite is called a moderator. Heavy water can also be used for this purpose.

heavier atoms. These particles possess very large energies, but how the energy is acquired is unknown. This so-called primary radiation interacts with the uppermost layers of air in the atmosphere with the production of secondary particles. These can be neutral, positively, or negatively charged. Some of the secondary radiation strikes the earth. Secondary radiation is subdivided into hard and soft components. The latter consist of photons and positive and negative electrons, and is called soft because it is not very penetrating. In contrast the hard component is very penetrating and can traverse large thicknesses of matter. The hard component is made up of mesons, which are unstable particles of mass intermediate between that of the electron and the proton.

The most familiar of the many types of meson known to exist are the π - and μ -mesons. The π -particle has a mass of about 273 times that of the electron, and can have either a positive or a negative charge.¹ A neutral particle (π^0) also exists. The three types of π -meson are highly unstable; the charged ones decay with a half-life of 2.65×10^{-8} second into a μ -meson and a neutrino. The uncharged meson decays with a half-life of about 5×10^{-14} second into two energetic photons. It is this decay of uncharged π -mesons that is thought to give rise in part to the soft component of cosmic rays.

The μ -meson which is produced by the decay of the π -meson has a mass about 216 times that of the electron. It is more stable than its parent, decaying with a half-life of 2.2×10^{-6} second into an electron and two neutrinos. An important difference between the π - and μ -mesons is that the π -meson has the power to interact with nuclei, occasionally breaking them into their constituent protons and neutrons. The interaction of μ -mesons on the other hand, is negligible. The bombardment of nuclei with high energy α -particles can result in the production of π - but not of μ -mesons. These facts make it likely that the π -meson is the one which is responsible for maintaining the stability of nuclei (§ 54).

The existence of τ -mesons, which have a mass about 1,000 times that of the electron and which decay into three π -mesons, is well established. The χ -meson of mass 1,100 times that of the electron and which decays into a μ -meson and two neutral particles has also been observed. There is some evidence for the existence of other types of mesons. It is possible that mesons at present thought to be different may later turn out to be identical; the apparent differences in properties may arise from the limitations of the experimental techniques used. In addition to mesons, particles (hyperons) heavier than the proton have been observed.

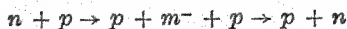
54. The Nucleus.—The particles in the nucleus are called collectively nucleons, and consist of protons and neutrons. The nucleus may be thought of as a sphere of radius about 2×10^{-13} cm. This shape suggests the analogy of a drop of liquid; the particles in the nucleus correspond to the molecules in the drop of liquid. A nucleus can exist in various energy states.

The nature of the forces holding the nucleons together is one of the main problems of modern physics. In order to account for the properties of nuclei it is necessary to assume that the nuclear force has a very short range, that it can overcome the considerable electrostatic repulsive forces that exist between the protons in the nucleus, and that it is of the exchange type (§ 80).

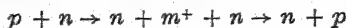
According to the theory first suggested by Yukawa in 1935, a pair of nucleons bound together by the nuclear force are attracted to one another

¹ Charged mesons (like protons and electrons) carry the unit electric charge (4.800×10^{-10} e.s.u.).

because they continually exchange their distinguishing characteristic, *i.e.*, their charge. The particles do this by transferring a meson which carries the charge back and forth between the bound particles according to the scheme:

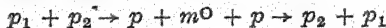
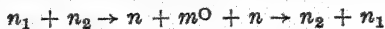


This shows that a neutron emits a negative meson which is transferred to a proton, with the result that the neutron has become a proton and the proton a neutron. Similarly the exchange



can take place.

Particles with a similar charge exchange an uncharged meson. The forces in this case are of a different nature from those mentioned above.



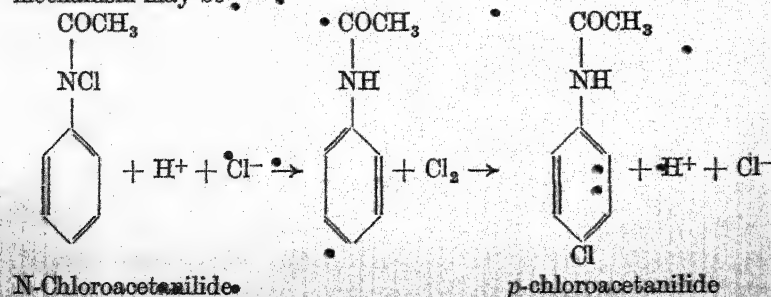
The continual exchange of mesons gives rise to an attractive force capable of maintaining the stability of the nucleus.

Yukawa's theory, which has undergone many changes since 1935, indicated that the nuclear force meson might make its appearance outside the nucleus. Yukawa also postulated that the meson should be unstable (to account for nuclear decay) and he calculated that the mass of the meson should be about 200 times that of the electron. The π -meson of cosmic rays has some properties of the nuclear force meson and it is attractive to identify the nuclear meson with the π -meson.

Though the meson theory has solved some of the difficulties of the nuclear force problem, and is therefore probably correct in outline, it fails to give complete agreement with experiment.

55. Use of Radio-Isotopes.—Radioactive isotopes have the same chemical properties as the corresponding non-radioactive element; as a result of this, radioactivity may be used as a tag which can be used to identify and follow the element through a series of reactions. This application of radioactivity, known as tracer technique, is used in chemical, biological and industrial studies. The following examples will illustrate the method.

(1) The transformation of N-chloroacetanilide to *p*-chloroacetanilide, which takes place in the presence of hydrochloric acid, may occur by two mechanisms. The first is an intramolecular mechanism in which the chlorine of the hydrochloric acid is not involved. Alternatively the mechanism may be



When hydrochloric acid which contained radioactive chlorine was used it was found that the *p*-chloroacetanilide obtained was radioactive. This indicated that a chlorine atom from the hydrochloric acid had substituted in the ring, and showed that the second mechanism was the one by which the reaction took place.

(2) Radioactive isotopes have been used in analytical work to test for completeness of precipitation. For example, a lead salt containing a known amount of a radioactive lead isotope is precipitated and the amount of radioactivity remaining in the solution is determined after evaporating the solution to dryness. This measurement will determine the amount of lead which is not precipitated from the solution.

(3) The absorption of phosphorus by a plant is another example of the application of tracer technique. If a phosphate containing a small quantity of radioactive phosphorus is fed to a plant the regions in which the greatest phosphorus absorption takes place can be determined photographically, as they will be the regions where the radioactivity is strongest. In a similar way nitrogen assimilation can be studied. For the study of photosynthesis radioactive carbon is employed. In medicine, the ultimate fate of substances taken orally can be determined, if certain parts of the molecule are "labelled" by radioactivity.

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CHAPTER III

ATOMIC STRUCTURE—PART II

56. **The Quantum Theory.**—To understand the origin of the quantum theory it is necessary to consider briefly the nature of radiation, of which one form is visible light. Newton regarded light as being made up of corpuscles, but this view was incapable of explaining many of the properties of light, such as interference, diffraction, and refraction. To give a satisfactory explanation of these phenomena, the wave-theory of light was formulated by Huygens. This assumed that light was a wave-motion, and did not involve the transfer of any material particle from one place to another. The colour of the light was dependent upon the wavelength. Fig. 37 represents an instantaneous state of a light wave; actually the wave is progressing all the time. The distance AB is the wavelength.¹ The theory was greatly developed by Clerk Maxwell, who propounded the electromagnetic theory of radiation, of which, however, no detailed account can be given here.

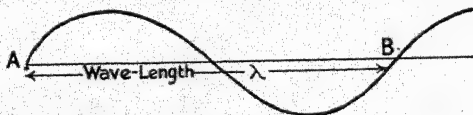


FIG. 37.

Although the wave-theory of light explained many facts in a very satisfactory way, and appeared to be firmly entrenched at the end of the nineteenth century, there were some phenomena for which it could offer no explanation, and the most troublesome of these was the problem of *black-body radiation*. In order to understand this, it is necessary to know that radiation includes not only visible light, but also many radiations that are invisible, including ultra-violet light, X-rays, infra-red light, and wireless waves. The range of wavelengths occupied by visible light is a very small fraction of the total range. All these radiations are wave-motions, but the wavelengths are different. The

¹The best definition of the term wavelength is the distance between two successive points of the wave with the same phase.

infra-red and wireless waves are of longer wavelength than ordinary visible light, whilst X-rays and ultra-violet light have smaller wavelengths. An idea of the range occupied by visible light is given in the following Table (XIII.).

TABLE XIII.—THE WAVELENGTHS OF RADIATIONS.

Radiation.	Wavelength Å.
Wireless waves	10^{14} to 4×10^7
Infra-red	3×10^6 to 7,230
Visible	7,230 to 3,970
Ultra-violet	3,970 to 500
X-ray and γ -rays	10 to 0.03

(1 Å = 10^{-8} cm.)

The wavelength ranges of the various radiations are not strictly defined, those given in the Table being approximate only.

Now, radiation is present in any space of which the temperature is greater than the absolute zero (-273.2°C.), and a vessel, closed all but for a very small hole, will give off radiation through the opening, dependent upon the temperature. It was shown by Kirchhoff that the radiation from such an enclosure is the same as that from a perfectly black surface, and it is known as black-body radiation.

The analysis of a given radiation into wavelengths is termed its *spectrum*. For a given temperature of emission, black-body radiation will have a definite spectrum, and the radiation of any specified wavelength emitted will possess a certain amount of energy. The energy distribution throughout the spectrum is not constant, but rises to a maximum at a certain wavelength for each temperature. The problem of black-body radiation was to reconcile the energy distribution in the spectrum with the wave-theory, but this was found to be quite impossible.

It was to overcome this difficulty, and others, that Max Planck boldly proposed the quantum theory, in a paper published in 1900. He showed that the experimental observations on black-body radiation could be explained by supposing that energy may be emitted or absorbed by a vibrating body, not continuously, but only in multiples of a certain unit, called a *quantum*. Furthermore, the size of the quantum of energy was proportional to the frequency of the radiation (velocity divided by

wavelength), and was therefore equal to $h\nu$, where ν is the frequency, and h a universal constant, known as Planck's constant, equal to 6.554×10^{-27} erg-seconds.

Let us see exactly what this means. The energy that is emitted in the form of radiation cannot be *any* amount of energy, but must be an integral number of quanta. The amount of energy in each quantum will be proportional to the frequency of the radiation, and, therefore, inversely proportional to the wavelength. The smaller the wavelength, the greater will be the frequency, and the greater the energy associated with each quantum. The quantum of X-rays, which have a very small wavelength, will therefore be greater than that of visible light. The size of the quantum for radiations of different wavelength is given in Table CIV, (Chapter XIX.).

The conception of the quantum of energy has not quite the same significance as that of the elementary particle of electricity, the electron. The electron always has the same charge, no matter where or how it occurs, but the quantum varies in size with the type of radiation with which it is associated, being comparatively large for X-rays and the ultra-violet, and small for the infra-red and wireless waves.

Since the quantum theory was proposed, numerous cases of the failure of the classical electromagnetic theory of Clerk Maxwell, which used the Newtonian mechanics, have been noted. The quantum theory has found its most useful application in explaining the phenomena connected with atomic structure.

57. Spectra.—Before proceeding further with the problem of atomic structure, we must note the various types of spectra that may be obtained, as a study of spectra has yielded most important results in the elucidation of the nature of matter.

When a body is heated from the absolute zero, it emits radiation. At low temperatures this is not visible. The body, if it were in a perfectly black space so that no radiation could get to it from the outside, would appear quite black. Nevertheless, it is giving off heat rays, which appear in the infra-red. As the temperature is raised, the solid begins to glow, and finally becomes incandescent, *i.e.*, it emits, amongst other radiation, visible light. If this light is examined by means of a spectrometer (for a description of which a text-book of Physics should be consulted), the spectrum is found to be continuous, *i.e.*, it is impossible to say where a colour begins or ends. There is a continuous gradation throughout the spectrum, from the violet end to the red. All incandescent solids show a continuous spectrum. The spectrum of the light from an electric lamp, for example, is a continuous one, because the light is emitted from an incandescent metal—the filament.

When the light emitted from incandescent gases and vapours is examined in the same way, it is found that the spectrum is now no

longer continuous, but consists of sharply defined lines in different colour regions of the spectrum. This is called a line-spectrum, and is characteristic of atoms. The spectrum may also consist of bands extending over a certain range of wavelength, separated by black bands. This is a band-spectrum, and is characteristic of molecules. The bands often show a periodic variation in intensity, and thus appear fluted.

The fact that when gaseous elements are raised to incandescence a line-spectrum is produced, has been known since about 1860, and has, of course, been applied in spectrum analysis to the characterisation of elements and the discovery of new ones. When sodium chloride is heated on a platinum wire, a yellow light is emitted, which on examination with the spectrometer, is found to possess a very simple structure, being made up of two lines very close together, of wavelengths 5889.965 \AA , and 5895.923 \AA . These lines are not the spectrum of incandescent sodium chloride, but that of sodium vapour. The heat of the flame dissociates the salt into its elements, and each atom emits separately. The chlorine is also radiating, but its spectrum is not observed with the spectrometer, as it falls outside the visible region, in the ultra-violet. That the yellow lines are indeed due to the sodium atom is shown quite clearly by the fact that they are obtained when any sodium salt is heated as described.

When the heat of a flame is not sufficient to break down the salt, an electric arc may be used. Thus, to obtain the spectrum of iron, the electric arc is passed between two iron rods, and the spectrum is examined. Such a spectrum is called an arc-spectrum, but is not quite so simple as that obtained by the previous method, as besides the normal iron atoms, there are also iron ions, produced by the arc, which themselves have a characteristic spectrum. An ion is produced from a normal atom by the removal of one or more electrons, thus leaving the atom positively charged.

To obtain the spectrum of a substance which is a gas at ordinary temperatures, *e.g.*, oxygen, the gas is enclosed in a discharge tube, and the electric discharge passed through it. Here, again, the spectrum obtained is not the simple line spectrum due to the atoms of oxygen alone. The passage of the discharge produces oxygen ions, which radiate their own spectrum, and there will also be the band spectrum due to oxygen molecules. The lines belonging to any one species can, however, be picked out in the spectrum.

All the types of spectra so far described are caused by the emission of radiation, and are classed under the general heading of emission spectra. There is, however, another type of spectrum of great importance, known as the absorption spectrum. When white light is passed through a coloured solution, or vapour, and the spectrum is then studied, it is found that there are black bands in the otherwise continuous spectrum.

The light of wavelength corresponding to the black bands has been absorbed by the substance through which the light has passed. The absorption spectrum is connected with the chemical constitution of the substance, and will be dealt with more fully in Chapters IX and XX.

58. The Quantum Theory and the Structure of the Atom.—Some two years after Rutherford had brought forward the nuclear theory of the atom, which we have already discussed (§ 29), Niels Bohr (1913) showed that this model of the atom was unstable, and could not exist. It will be remembered that, in the case of the Thomson model, the forerunner of the Rutherford nuclear atom, the electrons were supposed to be placed in a sphere of uniform positive electrification, and were at rest. Now this model is quite sound from the point of view of mechanics. It can be shown experimentally, that if one of the negative charges in this model is displaced from its position of rest, it will return to it again. The Rutherford atom, however, consists of a mass having a positive charge, with electrons revolving round it in a sort of solar system. Rutherford assumed that the same forces which keep the earth in its orbit round the sun would serve to keep the electron in its orbit round the nucleus. This simple view of the atom is too indefinite when examined from the quantitative point of view. The electron is not simply a solid body. It has an electrical charge. Clerk Maxwell had shown some time previously that when an electric charge is accelerated, radiation is emitted. Whenever a body moves in an orbit, it is being accelerated towards the centre of the orbit. This acceleration is shown by the existence of the centrifugal force. The electron, then, is being continually accelerated towards the centre of the orbit, and must therefore be emitting radiation. Since, according to the theory, the motion is uniform, the spectrum should show no discontinuities, and the spectrum of an incandescent atom should be continuous. It is actually discontinuous. The Rutherford theory, then, fails to explain the facts.

Bohr propounded a theory which offered an explanation of this discrepancy, and is based on Planck's conception of the quantum. There are two fundamental suppositions. They are:—

(1) For each atom there is a series of orbits in which the electrons rotate, but no radiation is emitted. These are called *stationary states*. It must not be thought that the electrons are stationary; they are not, but the effect is as if they were, for no radiation is given out. A stationary state is characterised by the fact that the angular momentum

of the electron is an integral multiple of $\frac{h}{2\pi}$, where h is Planck's constant.

This is an extension of the original conception of Planck in quantising the energy of a vibrator.

In order that the student may make himself thoroughly familiar with this first assumption, we may use it to calculate the radii of the permitted orbits in the hydrogen atom. In the hydrogen atom, we have one electron and one proton. Let the charge on the electron be $-e$, and its velocity, v cm. per sec. If the orbit is supposed circular, and of radius r , the centrifugal force, F_1 , is given by

$$F_1 = \frac{mv^2}{r}.$$

This must be equal to the force of attraction between the proton and the electron, which is given by Coulomb's inverse square law

$$F_2 = \frac{e^2}{r^2},$$

assuming that this Law is still true at atomic distances and that the dielectric constant of the medium is unity.

Hence
$$\frac{mv^2}{r} = \frac{e^2}{r^2},$$

or

$$e^2 = mv^2r \quad (1).$$

According to Bohr's assumption, the angular momentum of the electron

is always some integral multiple of $\frac{h}{2\pi}$. Hence

$$mvr = \frac{nh}{2\pi} \quad (2)$$

From (2)

$$v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2}.$$

Substituting in (1),

$$e^2 = \frac{n^2 h^2}{4\pi^2 m r},$$

or

$$r = \frac{n^2 h^2}{4\pi^2 m e^2}.$$

Since every quantity on the right-hand side of this expression, with the exception of n , is fixed, it follows that the radii of the permitted orbits are proportional to the squares of the natural numbers. By substituting the accepted values of h (6.62×10^{-27} erg-seconds), m (9.1×10^{-28}

gm), and e (4.802×10^{-10} e.s.u.), and making $n = 1, 2, 3$, etc., we obtain the radii of the orbits:—

$$r_1 = 0.53 \times 10^{-8} \text{ cm.}, r_2 = 2.12 \times 10^{-8} \text{ cm.}, \text{ etc.}$$

There are so many assumptions in this calculation that it probably has no physical significance, but it is merely given to illustrate the meaning of the first Bohr postulate.

(2) The second assumption is that when an electron passes from one orbit, of energy E_1 , to another of energy E_2 , monochromatic radiation (i.e., radiation of one wavelength only) of frequency ν is emitted or absorbed, equal in amount to $h\nu$. Thus, when an electron rotating in one of the stationary states suddenly jumps to another, of less energy, the difference in the energy is given out in the form of monochromatic radiation. The reverse process takes place when energy is absorbed. The absorption of radiation results in the transfer of an electron from a level of low to one of higher energy content. The mathematical expression of this assumption is

$$E_1 - E_2 = h\nu.$$

It must be remembered that these two assumptions are separate and distinct. The first has to deal with the energy of the rotating electron, the second with the energy difference between two states.

The term *energy level* is frequently used to denote a stationary state, and the energy content is defined by a *quantum number*. The level of quantum number 1 has least energy.

To clarify our ideas on the emission and absorption of energy by an atom, consider what happens to say, hydrogen atoms when they are submitted to the electric discharge. They first of all absorb energy from the discharge, and this moves the electrons from an inner energy level, of low energy, to outer ones of higher energy. The electrons then return to the form containing lowest energy (for, of all systems, that which possesses the least energy is the most stable) by jumps, passing through intermediate energy levels, or perhaps by only one jump. Each transition is accompanied by a liberation of energy in the form of radiation, and as each emission is monochromatic, lines in the spectrum will result. This explains the line spectrum of the atoms.

59. The Spectrum of Hydrogen.—It is now necessary to study a subject which in itself is purely physical, and which at first sight would seem to be of no interest at all to the physical chemist. Yet a study of the spectrum of hydrogen has yielded results of extraordinary importance in connection with the structure of the atom.

As far back as 1885, Balmer noticed that the wavelengths of certain lines in the hydrogen spectrum were related to each other in a simple

manner, and could be expressed by a general formula. In this connection we shall deal not with the wavelength, but with its reciprocal, which is called the *wave-number*. It is the number of vibrations per cm., and may be denoted by ν_0 . ν_0 is often loosely called a frequency.

Balmer's formula, which gives the frequencies of some of the hydrogen lines may be expressed in the form

$$\nu_0 = 109678.8 \left(\frac{1}{2^2} - \frac{1}{m^2} \right),$$

where m can have any integral value greater than 2. As m approaches ∞ , the lines will get closer and closer, and approach a limit known as the

convergence frequency. This frequency is obviously $\frac{109678.8}{4}$ i.e.,

27419.7. The following Table shows how closely the observed and calculated wave-numbers agree.

TABLE XIV.—BALMER'S SERIES

$$\nu_0 = 109678.8 \left(\frac{1}{2^2} - \frac{1}{m^2} \right)$$

m .	ν_0 calc.	ν_0 obs.
3	15233.2	15233.2
4	20564.8	20564.8
5	23032.5	23032.5
6	24373.0	24373.1
7	25181.4	25181.3
8	25706.0	25706.0
20	27145.5	27145.2
∞	27419.7	—

Other series in the spectrum of hydrogen have since been discovered which are governed by exactly similar formulæ. Thus, Lyman found that a certain series in the hydrogen spectrum could be expressed by the equation

$$\nu_0 = 109678.8 \left(\frac{1}{1^2} - \frac{1}{m^2} \right).$$

This series of lines is in the far ultra-violet. A similar series in the infra-red, for which the formula was discovered by Paschen, is governed by

$$\nu_0 = 109678.8 \left(\frac{1}{3^2} - \frac{1}{m^2} \right).$$

Another series was discovered by Brackett, and is governed by

$$\nu_0 = 109678.8 \left(\frac{1}{4^2} - \frac{1}{m^2} \right).$$

All these series are called after the names of their discoverers, the Balmer, Lyman, Paschen and Brackett series. Actually there is one formula which will express them all, viz.,

$$\nu_0 = \frac{109678.8}{n^2} - \frac{109678.8}{m^2}.$$

In the Lyman series, $n = 1$, and $m = 2, 3, 4$, etc.

In the Balmer series, $n = 2$, and $m = 3, 4, 5$, etc.

In the Paschen series, $n = 3$, and $m = 4, 5, 6$, etc.

In the Brackett series, $n = 4$, and $m = 5, 6, 7$, etc.

The two sections of the above equation are called *terms*. Thus $109678.8/n^2$ is one term, whilst $109678.8/m^2$ is the other. It has been found that all spectra, not only of hydrogen, but of all elements, can be expressed as a difference of two terms similar in form to the above.

It is evident from this formula, that if we write down the values of the first term when $n = 1, 2, 3, 4$, etc., then, if we subtract the second, third, fourth, etc., terms from the first, we get the Lyman series; if we subtract the third, fourth, fifth, etc., from the second, we get the Balmer series; if we subtract the fourth, fifth, sixth, etc., from the third, we get the Paschen series; and if we subtract the fifth, sixth, seventh, etc., from the fourth, we get the Brackett series. This is shown in the following Table (XV.).

TABLE XV.—HYDROGEN SERIES

m^2	Term.	Lyman. $n = 1$ $m = 2, 3, 4 \dots$	Balmer. $n = 2$ $m = 3, 4, 5 \dots$	Paschen. $n = 3$ $m = 4, 5, 6 \dots$	Brackett. $n = 4$ $m = 5, 6, 7 \dots$
1	109678.8				
2	27419.7	82259.1			
3	12186.5	97492.3	15233.2		
4	6854.9	102823.9	20564.8	5331.6	
5	4387.2	105291.6	23032.5	7799.3	2467.7
6	3046.7	106632.1	24373.0	9139.8	3808.2
7	2238.3	107440.5	25181.4	9948.2	4616.6
8	1713.7	107965.1	25706.0	10472.8	5141.2
∞	0	109678.8	27419.7	12186.5	6854.9

The fact that so many spectral lines, which at first sight seem to be totally unrelated, can be reduced to order in this simple way, is a remarkable fact; and when we consider that this has now been done for the spectra of almost all elements, though not with the same completeness as for hydrogen, it is seen what a wealth of information we possess in connection with spectra. It is to be expected that such a simple relationship between the spectral lines must have some relatively straightforward explanation. It has, and it will be shown later how this explanation is bound up with the structure of the atom.

The mathematical expression for a series of spectral lines of an element is not always as simple as that for hydrogen though it is usually not much more complex. According to the Ritz combination principle the wave number of any spectral line may be represented as the combination of two terms, one of which is constant and the other variable throughout a spectral series. The wave number of any spectral line may be expressed by

$$\nu_o = \frac{R}{x^2} - \frac{R}{y^2}$$

x and y are integers for the lines in the hydrogen series, but not necessarily so for the spectra of other atoms.

60. The Theory of the Hydrogen Spectrum.—Bohr's assumptions as regards the structure of the atom have already been noted (§ 58). These may now be studied a little more closely.

The first assumption of Bohr was that the angular momentum of the electron was always an integral multiple of $\frac{h}{2\pi}$. Assuming that the

electron travels in a circular orbit, and that its mass is m , its velocity v , and the radius of the orbit r , then its angular momentum is mvr , and the above assumption can be expressed in the form

$$mvr = \frac{n\hbar}{2\pi} \quad (1)$$

where n is any integer.

If Z is the atomic number of the element, and the charge on the nucleus is Ze , the potential energy of the electron will be $\frac{-Ze \cdot e}{r} = \frac{-Ze^2}{r}$. The negative sign is prefixed because work is done on the system when the electron is removed from the nucleus to an infinite distance.

The kinetic energy of the electron is $\frac{1}{2}mv^2$. Assuming that the law of

force between the nucleus and the electron is the inverse square law, and that the proportionality factor is unity, then the force between the nucleus and the electron will be $\frac{Ze^2}{r^2}$.

The acceleration of the electron towards the centre of the orbit is v^2/r , and the force on it is therefore mv^2/r .

Hence
$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}, \quad (2)$$

and the kinetic energy

$$\frac{1}{2}mv^2 = \frac{Ze^2}{2r}. \quad (3)$$

The total energy of the atom is the sum of the potential and kinetic energies, and is therefore

$$-\frac{Ze^2}{r} + \frac{Ze^2}{2r} = -\frac{Ze^2}{2r} = -\frac{1}{2}mv^2.$$

From (1)

$$\frac{1}{2}mv = \frac{nh}{4\pi r}.$$

Dividing into (3)

$$v = \frac{Ze^2 \cdot 2\pi}{nh}.$$

The total energy is therefore

$$E_n = -\frac{1}{2}mv^2 = -\frac{2\pi^2 Z^2 me^4}{n^2 h^2}; \text{ or } E_n = -E_\infty = -\frac{2\pi^2 Z^2 me^4}{h^2} \cdot \frac{1}{n^2}, \quad (4)$$

where E_∞ is the work which must be done on the system to remove the electron to infinity, and is therefore a measure of the stability of the system. The larger is E_∞ , the more stable will the system be. For large values, n must be as small as possible; hence the most stable orbit is that in which n is unity.

We can now apply the second postulate of Bohr, viz., that when an electron jumps from one orbit to another energy is given out as a quantum of radiation. If it jumps from an outer (n_2) to an inner (n_1) orbit, energy is given out in the form of monochromatic radiation of which the frequency is given by

$$h\nu = E_{n_2} - E_{n_1}.$$

This amount of energy must be the difference in the energy associated with the orbits and worked out as above. Hence

$$h\nu = \frac{2\pi^2 Z^2 me^4}{h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right). \quad (5)$$

Now, ν is a frequency. It is easily seen that to bring this to wave-

numbers, which are given by the equation $\nu_0 = \frac{\nu}{c}$, where c is the velocity of light, we must divide the frequency by the velocity of light, c . If ν_0 now represents wave-number,

$$\nu_0 = \frac{2\pi^2 Z^2 m e^4}{c h^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (6)$$

This expression is identical in form with the Balmer formula, and when the value of the constant $\frac{2\pi^2 Z^2 m e^4}{c h^3}$ is worked out, it is found to agree with the Rydberg constant.

Thus, substituting the value for $e = 4.802 \times 10^{-10}$ e.s.u., $h = 6.624 \times 10^{-27}$ erg sec., $c = 2.9977 \times 10^{10}$ cm. per sec., and $m = 9.107 \times 10^{-28}$ gm., we have, for hydrogen, $Z = 1$,

$$\begin{aligned} \frac{2\pi^2 Z^2 m e^4}{c h^3} &= \frac{2\pi^2 \times 9.107 \times 10^{-28} \times (4.802 \times 10^{-10})^4}{2.9977 \times 10^{10} \times (6.624 \times 10^{-27})^3} \\ &= 109,700, \end{aligned}$$

which agrees quite well with the Rydberg constant determined experimentally, 109,678.

It is known that in the Lyman series, $n_1 = 1$. Referring to the mode of derivation of equation (6) it is clear that this means that the lines of this series are due to transitions ending at the first orbit, the level of least energy. Thus, the Lyman series will be emitted when, energy having been imparted to the hydrogen atoms by the electric discharge, or some other means, they revert from the higher energy levels to which they have been raised to the first, or lowest energy level. The Balmer series has $n_1 = 2$, so the lines are due to electrons falling back to the second energy level. In the Paschen series $n_1 = 3$, and in the Brackett series $n_1 = 4$, so that here the electrons are returning from some outer orbit to which they have been removed by the excitation, to the third and fourth energy levels, respectively.

This remarkably simple and accurate formulation of the hydrogen spectrum points to the accuracy of the postulates upon which it is based, viz., Bohr's quantum model.

It is seen that the term numbers are really measures of energy. They represent the energy which would be required to remove an electron from the orbit which they represent to infinity ($n_2 = \infty$). The greatest term number is that obtained when $n_1 = 1$, and is therefore called the "ground" term. The electron can be removed to infinity, i.e., the gas can be ionised, by several means, but particularly by subjecting the gas to bombardment by electrons. In an ideal case, supposing the loss of no energy whatever, the energy associated with the bombarding electron,

which is just capable of knocking the electron from the ground state to infinity, must be the energy of that electron which is removed. Hence, if we can measure the energy of the electrons which will just ionise the gas, we have another measure of the energy of the electron in the atom. The energy associated with a bombarding electron is always measured by the potential which is used to accelerate it. The energy of the electron depends upon its velocity, being given, in fact, by the product of the charge and the accelerating potential through which it has passed. As the charge of the electron is always the same, it is sufficient to specify the accelerating potential which is given to the electron when it is desired to denote its energy. The ionisation potential of hydrogen is the potential through which a bombarding electron has to be accelerated in order to remove an electron from the atom to infinity. What this value should be for the ground term of hydrogen is readily obtained as follows. Let V be the ionisation potential, ν_0 the wave-number of the ground term, c the velocity of light, h Planck's constant, and e the charge on the electron. The energy associated with the term is $h\nu$ or $ch\nu_0$. The energy is *potential* \times *charge*, hence the ionisation potential is given by

$$V = \frac{\text{energy}}{\text{charge}} = \frac{ch\nu_0}{e}.$$

This must be multiplied by 10^{-8} to bring the absolute units to volts, and by c to convert into electromagnetic units. So we have

$$V = \nu_0 \frac{c^2 h}{e} \times 10^{-8} = \frac{\nu_0}{8,100}.$$

For hydrogen, $\nu_0 = 109,678$, and substituting the other figures, we have

$$V = \frac{109,678}{8,100},$$

which gives

$$V = 13.54 \text{ volts.}$$

The ionisation potential of hydrogen is therefore 13.54 volts, for removal of the electron from the ground term. Corresponding ionisation potentials are known for removal of ions from the other levels. In all cases the observed values agree well with those calculated.

The diagram (Fig. 38) shows the stationary states of the hydrogen atom, assuming that the orbits are circular. Another way of representing the facts is by means of the energy diagram given in Fig. 39.

61. General Theory of Spectra.—Hydrogen, the atom of which consists of one proton and a single electron, is the simplest instance to consider. When the other elements, which contain larger numbers of electrons, are dealt with, the difficulties are considerably increased.

With hydrogen, it is only a question of the removal of one electron into any desired stationary state, but with other atoms some of the innermost levels may be permanently filled with electrons. What happens in this case? If an electron is expelled from the innermost level altogether,

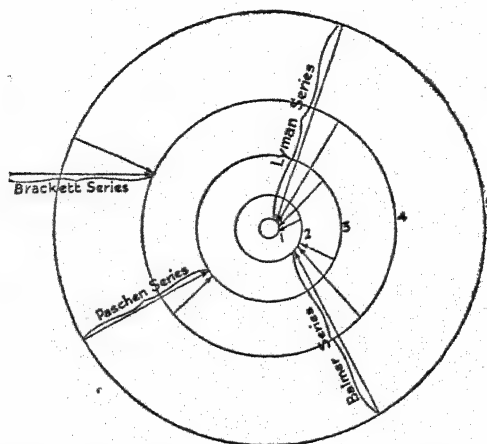


FIG. 38.—Stationary States in the Hydrogen Atom assuming circular orbits.

(The radii of the orbits are proportional to 1, 4, 9, 16 . . .)

its place is immediately occupied by an electron from one of the higher levels, and this goes on through successive levels, until the loss is really felt only in the outer level. If the electron is only removed to a level one or two higher in quantum number, then an electron from that level immediately falls back into the place previously occupied.

The amount of energy associated with the innermost levels is so great that when an electron is expelled from these levels the frequency of the radiation emitted is very great. Thus $E = h\nu$, is large, and therefore ν , the frequency of the emitted radiation, is great, and such a transition gives rise to X -rays which are similar to ordinary light, but have exceedingly small wavelengths, and correspondingly great frequencies. The study of these X -ray spectra of the elements has given us a great deal of information about the structure of the atom. Indeed, it was by the aid of these spectra that Moseley fixed the atomic numbers of the elements (§ 37).

The X -rays obtained from elements are grouped in wavelengths in certain groups which have been called the K , L , M , N , etc., groups. These groups are known to be due to transitions which end at the quantum levels 1, 2, 3, 4, etc., respectively. It is for this reason that the

quantum levels themselves are frequently called the *K*, *L*, *M*, *N*, etc., levels.

From a study of the *X*-ray spectra the number of electrons present in each level can be roughly derived. All atoms will give a *K* radiation, only those heavier than sodium give the *L* radiation, and so on.

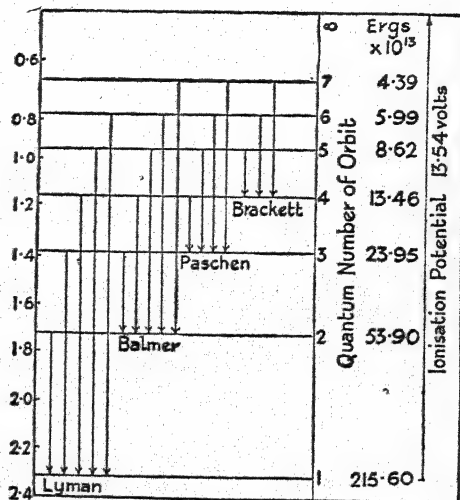


FIG. 39.—Energy Diagram for Hydrogen.
The arrows represent transitions from the various orbits.

62. Elliptical Orbits.—The spectrum of hydrogen has been explained by assuming that the electron in hydrogen moves in a circular orbit about the nucleus, and that the energy of the electron in an orbit is defined by a quantum number n . The energy of the electron depends on the distance of the electron from the nucleus and hence the quantum number n defines the radius of an orbit.

The more complicated spectra of the higher elements can only be described satisfactorily by assuming that the electrons move in elliptical orbits, the nucleus of the atom being situated at one of the foci of the orbits. This conception of elliptical orbits was introduced by Sommerfeld in 1915. The energy of an electron in an elliptical orbit depends on two quantum numbers n and l ; both are integral. The number n in the Sommerfeld theory defines the length of the major axes of the elliptical orbit; the second quantum number l defines the length of the minor axis and hence the ellipticity of the orbit. Elliptical orbits are permitted in any atom, even hydrogen, in addition to circular orbits; the orbits permitted are subject to the requirements of classical mechanics and the simple quantisation principle as applied by Bohr to circular orbits only.

In the hydrogen atom, because the centre of attraction is simply the nucleus of the atom, the energy of an electron depends only on the size of the major axes of the ellipse and not on the ellipticity. Therefore, the need for the second quantum number l is not evident from the ordinary spectroscopic data for the hydrogen atom. However, in an atom containing many electrons the energy of an electron in an outer orbit does depend on the ellipticity of the orbit because the degree to which it penetrates into the shell of inner electrons depends on this. Hence the energy of such an electron depends not only on the value of n for the orbit in which it is moving but also on the value of l ; thus n defines a principal energy level within the atom; l defines a sub-energy level within the principal level. For any value of n , l can have values ranging from $l = n$ to $l = 1$; $l = n$ corresponds to a circular orbit, while $l = 0$ would mean that the minor axis is equal to 0 and hence the ellipse would have degenerated to a straight line. Therefore, it is deduced from the theory of elliptical orbits that for each value of n there should be n values for l ; that is the integral numbers from $l = n$ to $l = 1$. The spectroscopic observations do in fact show that for each value of n there are n values for l ; but the n possible values of l found are those ranging from $l = 0$ to $l = n - 1$; thus the observations indicate an orbit (the one corresponding to $l = 0$) that does not appear possible in the model of the atom developed by the theory. This fact represents a fundamental weakness in the theory of elliptical orbits. The Sommerfeld theory does, however, represent an advance on the Bohr theory in that it explains the existence of sub-energy levels for electrons in each of the principle energy levels of the atom. It does not explain all the experimental facts because as mentioned it fails to give the values of the quantum number l that are deduced experimentally. The theory has now been discarded in favour of a new approach, the wave mechanical theory.

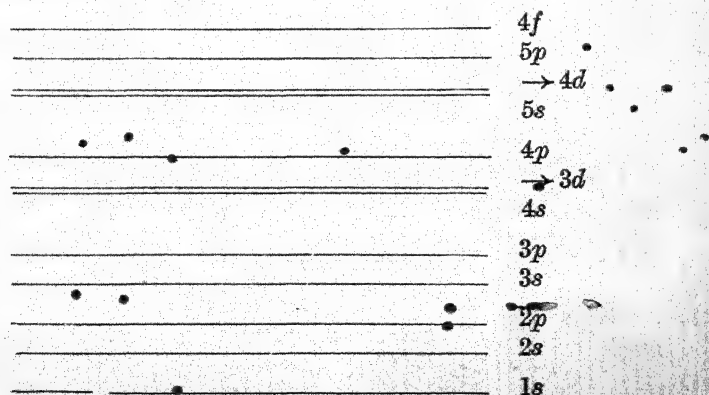


FIG. 40.—Energy Levels.

As stated previously, corresponding to each principle energy level defined by a value of the quantum number n there are n sub-states which are defined by a quantum number l . This may have integral values from 0 to $n - 1$. The energy state corresponding to $l = 0$ is called an s state; that corresponding to l equal to 1 is called a p state; to $l = 2$ a d state; to $l = 3$ an f state. For higher values of l the letters in the alphabet following f are used; g represents $l = 4$, h represents $l = 5$ and so on. In naming a particular state the principal quantum number is followed by the letter designating the value of l . Thus the energy state $n = 1$; $l = 0$ is called the $1s$; the state $n = 2$, $l = 1$ is the $2p$ state. The series of possible energy levels in an atom is shown in the accompanying diagram (Fig. 40) in order of increasing energy. As will be observed from this figure the energy depends mainly on the value of n .

63. The General Nature of Spectra.—As a rule, the arc or spark spectrum of an element contains four sets of lines which are distinguished by their nature. They are called the Sharp, Principal, Diffuse and Fundamental series. The Sharp series is made up of clear-cut thin lines. The Principal series is usually the brightest. The Diffuse series is made up of diffuse lines, *i.e.*, lines without very definite edges. The Fundamental series is rather badly named, as it is not by any means fundamental.¹ Sometimes the Diffuse is called the First Subordinate series, and the Sharp the Second Subordinate series, though the names first given are more usually used.

These series are simply related to each other, and are usually referred to by the initial letter of the name, *i.e.*, the S , P , D and F spectra.

TABLE XVI.—SHARP AND PRINCIPAL SERIES OF LITHIUM

Sharp Series				Principal Series			
$\nu_0 = 28,611 - \frac{109,737}{(m + 0.590)^2}$				$\nu_0 = 43,477 - \frac{109,737}{(m + 0.959)^2}$			
$= 28,611 - mS$				$= 43,477 - mP$			
$= 1P - mS$				$= 1S - mP$			
m	mS	ν calc.	ν obs.	m	mP	ν calc.	ν obs.
1	43,407	—	—	1	28,594	14,883	14,904
2	16,359	12,252	12,302	2	12,533	30,944	30,926
3	8,515	20,096	20,107	3	7,001	36,476	36,468
4	5,209	23,402	23,395	4	4,462	39,015	39,013
5	3,512	25,099	25,082	5	3,091	40,386	40,387
6	2,527	26,084	26,047	6	2,266	41,211	41,213
∞	—	28,611	—	∞	—	43,477	—

¹ This series is also sometimes known as the Bergmann series.

They are also expressed by formulæ similar to the Rydberg formula. The Table below gives the Sharp and Principal series of lithium.

It is to be noted that the convergence frequency of the Sharp series (obtained by putting m equal to infinity), is almost equal to the first term of the Principal sequence,¹ and that similarly the first term of the Sharp sequence is almost equal to the convergence frequency of the Principal series. There are numerous relationships of this kind which have all received satisfactory explanation on the quantum model of the atom. If we call the successive terms of the Principal sequence $1P$, $2P$, $3P$, $4P$. . . mP , of the Diffuse sequence $1D$, $2D$, $3D$, $4D$, . . . mD , and similarly for the other sequences, these relationships can be summed up in the equations:—

Sharp Series	$\nu_0 = 1P - mS$
Principal Series	$\nu_0 = 1S - mP$
Diffuse Series	$\nu_0 = 1P - mD$
Fundamental Series	$\nu_0 = 1D - mF$

It will be seen that these relationships express what has been already discovered with regard to the convergence frequencies of the Sharp and Principal series, and they also show that the convergence frequency of the Fundamental series is the first term of the Diffuse sequence.

Many of the lines in a spectrum can be explained in this way, but there are some which are still unaccounted for. These are combination lines formed from terms from different sequences. It is not possible for lines to exist derived from any combination of terms at choice. There is an important selection principle which forbids certain combinations. If the terms are arranged in the order S , P , D , F , then the combination lines must always be due to terms taken from two adjacent sequences. Lines of the nature $3D - mF$ could exist, but not lines derived from $2P - mF$.

64. Multiplets in the Spectrum.—If the lines of a spectrum are very carefully examined with a spectroscope which gives high resolution, it is found that the lines are not single, but are made up of a number of lines very close together. Sometimes there are only two. These are called doublets. If there are three they are called triplets; and in general they are called multiplets.

If the wave-numbers of the first few members of the Sharp series of sodium are written down, it is found that they consist of doublets with a constant separation between each.

Similarly, the Principal series of sodium is made up of doublets, but here the separation is not constant, but diminishes as we pass towards the ultra-violet, both series having the same convergence limit.

¹ The word "series" is used when referring to observed lines, and "sequence" when referring to terms.

TABLE XVII.—SODIUM DOUBLETS IN THE SHARP SERIES

m	ν_1	ν_2	$\nu_2 - \nu_1$
3	16,231	16,248	17
4	19,404	19,421	17
5	21,043	21,060	17
6	21,997	22,013	16

TABLE XVIII.—RUBIDIUM DOUBLETS IN THE DIFFUSE SERIES

ν_1	ν_2	$\nu_2 - \nu_1$
12,887	13,121	234
15,872	16,107	235
17,463	17,699	236
18,405	18,641	236

The explanation of this lies in the fact that there are two sets of P terms, but only one of S terms, so that if the two P terms are represented by P_1 and P_2 , the Sharp series will be given by

$$\nu_1 = 1P_1 - mS$$

$$\nu_2 = 1P_2 - mS$$

The separation is thus constant and equal to $1P_1 - 1P_2$.

For the Principal series, however,

$$\nu_1 = 1S - mP_1$$

$$\nu_2 = 1S - mP_2$$

Here the difference involves m , and so varies, until, when m is equal to infinity, the convergence limit is $1S$. The same type of relationship holds for the Diffuse and Fundamental series, but it is always found that there is only one set of S terms, whilst the P , D and F terms may be complex, and give rise to multiplets.

In order to explain the existence of spectral multiplets Uhlenbeck and Goudsmit suggested that the electron spins about its axis and that the spin energy contributed to the electronic energy. The spin energy, like the rest of the electronic energy is quantised. The energy depends on a spin quantum number s , which can have two values $+\frac{1}{2}$ and $-\frac{1}{2}$.

TABLE XIX.—ELECTRONIC STRUCTURES OF THE ELEMENTS

The transitional elements are in bold type; the rare earth elements are in italics.

Shell		K	L		M			N			
Element	Atomic Number	$n = 1$	2		3			4			
		$l = 0$ State 1s	0 2s	1 2p	0 3s	1 3p	2 3d	0 4s	1 4p	2 4d	3 4f
H	1	1									
He	2	2									
Li	3	2	1								
Be	4	2	2								
B	5	2	2	1							
C	6	2	2	2							
N	7	2	2	3							
O	8	2	2	4							
F	9	2	2	5							
Ne	10	2	2	6							
Na	11	2	2	6	1						
Mg	12	2	2	6	2						
Al	13	2	2	6	2	1					
Si	14	2	2	6	2	2					
P	15	2	2	6	2	3					
S	16	2	2	6	2	4					
Cl	17	2	2	6	2	5					
A	18	2	2	6	2	6					
K	19	2	2	6	2	6		1			
Ca	20	2	2	6	2	6		2			
Sc	21	2	2	6	2	6	1	2			
Ti	22	2	2	6	2	6	2	2			
V	23	2	2	6	2	6	3	2			
Cr	24	2	2	6	2	6	4	2			
Mn	25	2	2	6	2	6	5	2			
Fe	26	2	2	6	2	6	6	2			
Co	27	2	2	6	2	6	7	2			
Ni	28	2	2	6	2	6	8	2			
Cu	29	2	2	6	2	6	9	2			
Zn	30	2	2	6	2	6	10	2			
Ga	31	2	2	6	2	6	10	2	1		
Ge	32	2	2	6	2	6	10	2	2		
As	33	2	2	6	2	6	10	2	3		
Se	34	2	2	6	2	6	10	2	4		
Br	35	2	2	6	2	6	10	2	5		
Kr	36	2	2	6	2	6	10	2	6		

TABLE XIX (continued)

Shell		K	L	M	N				O				P
Element	Atomic Number	$n = 1$	2	3	4				5				6
		$l =$ State			0 4s	1 4p	2 4d	3 4f	0 5s	1 5p	2 5d	3 5f	0 6s
Rb	37	2	8	18	2	6			1				
Sr	38	2	8	18	2	6			2				
Y	39	2	8	18	2	6	1		2				
Zr	40	2	8	18	2	6	2		2				
Nb	41	2	8	18	2	6	3		2				
Mo	42	2	8	18	2	6	4		2				
Tc	43	2	8	18	2	6	5		2				
Ru	44	2	8	18	2	6	6		2				
Rh	45	2	8	18	2	6	7		2				
Pd	46	2	8	18	2	6	8		2				
Ag	47	2	8	18	2	6	9		2				
Cd	48	2	8	18	2	6	10		2				
In	49	2	8	18	2	6	10		2	1			
Sn	50	2	8	18	2	6	10		2	2			
Sb	51	2	8	18	2	6	10		2	3			
Te	52	2	8	18	2	6	10		2	4			
I	53	2	8	18	2	6	10		2	5			
Xe	54	2	8	18	2	6	10		2	6			
Cs	55	2	8	18	2	6	10		2	6			1
Ba	56	2	8	18	2	6	10		2	6			2
La	57	2	8	18	2	6	10		2	6	1		2
Ce	58	2	8	18	2	6	10	1	2	6	1		2
Pr	59	2	8	18	2	6	10	2	2	6	1		2
Nd	60	2	8	18	2	6	10	3	2	6	1		2
Pm	61	2	8	18	2	6	10	4	2	6	1		2
Sm	62	2	8	18	2	6	10	5	2	6	1		2
Eu	63	2	8	18	2	6	10	6	2	6	1		2
Gd	64	2	8	18	2	6	10	7	2	6	1		2
Tb	65	2	8	18	2	6	10	8	2	6	1		2
Ds	66	2	8	18	2	6	10	9	2	6	1		2
Ho	67	2	8	18	2	6	10	10	2	6	1		2
Er	68	2	8	18	2	6	10	11	2	6	1		2
Tm	69	2	8	18	2	6	10	12	2	6	1		2
Yb	70	2	8	18	2	6	10	13	2	6	1		2
Lu	71	2	8	18	2	6	10	14	2	6	1		2
Hf	72	2	8	18	2	6	10	14	2	6	2		2
Ta	73	2	8	18	2	6	10	14	2	6	3		2
W	74	2	8	18	2	6	10	14	2	6	4		2

TABLE XIX (continued)

Shell		K	L	M	N	O				P			Q
Element	Atomic Number	n = 1	2	3	4	5				6			7
		l = State				0	1	2	3	0	1	2	0
						5s	5p	5d	5f	6s	6p	6d	7s
Re	75	2	8	18	32	2	6	5		2			
Os	76	2	8	18	32	2	6	6		2			
Ir	77	2	8	18	32	2	6	7		2			
Pt	78	2	8	18	32	2	6	8		2			
Au	79	2	2	18	32	2	6	9		2			
Hg	80	2	8	18	32	2	6	10		2			
Tl	81	2	8	18	32	2	6	10		2	1		
Pb	82	2	8	18	32	2	6	10		2	2		
Bi	83	2	8	18	32	2	6	10		2	3		
Po	84	2	8	18	32	2	6	10		2	4		
At	85	2	8	18	32	2	6	10		2	5		
Rn	86	2	8	18	32	2	6	10		2	6		
Fr	87	2	8	18	32	2	6	10		2	6		1
Ra	88	2	8	18	32	2	6	10		2	6		2
Ac	89	2	8	18	32	2	6	10		2	6	1	2
Th	90	2	8	18	32	2	6	10	1	2	6	1	2
Pa	91	2	8	18	32	2	6	10	2	2	6	1	2
U	92	2	8	18	32	2	6	10	3	2	6	1	2
Np	93	2	8	18	32	2	6	10	4	2	6	1	2
Pu	94	2	8	18	32	2	6	10	5	2	6	1	2
Am	95	2	8	18	32	2	6	10	6	2	6	1	2
Cm	96	2	8	18	32	2	6	10	7	2	6	1	2
Bk	97	2	8	18	32	2	6	10	8	2	6	1	2
Cf	98	2	8	18	32	2	6	10	9	2	6	1	2
	99	2	8	18	32	2	6	10	10	2	6	1	2
	100	2	8	18	32	2	6	10	11	2	6	1	2
	101	2	8	18	32	2	6	10	12	2	6	1	2
	102	2	8	18	32	2	6	10	13	2	6	1	2
	103	2	8	18	32	2	6	10	14	2	6	1	2
	104	2	8	18	32	2	6	10	14	2	6	2	2
	105	2	8	18	32	8	6	10	14	2	6	3	2

There are now three quantum numbers to describe the energy of an electron in an atom. The spin energy is very small; so if we consider an electron in a p level it can have one of two values of spin energy. A transition from the p level to a lower level in the atom will produce two lines corresponding to the two different changes in energy. Because the initial levels are very close together the lines corresponding to the transitions are also very close and they appear as one line except when observed under high resolution.

65. Magnetic Quantum Numbers.—It has been observed that if a spectral source is placed in a strong magnetic field and the spectrum is observed at right angles to the field, the spectral lines, which are single in the absence of the magnetic field, will split into a number of lines. In order to explain this effect it is necessary to introduce a fourth quantum number, m , to allow for the energy level states an electron may take up in a magnetic field. This fourth quantum number may have integral values from l to 0 to $-l$ for any l value. In other words there are $2l + 1$ values of m for each l value; that is there are $2l + 1$ energy states each corresponding to a different value of m . The number of m values gives the number of ways in which an electron can orient itself in a magnetic field.

We can see, therefore, that to account for atomic spectra it is necessary to assume that each energy state of an electron is defined by four quantum numbers:

n , which is an integer;

l , which for any value of n can have integral values from 0 to $n - 1$;

m , which for any value of l can have integral values $-l$ to $+l$;

and finally s , which can have one of two values $\pm \frac{1}{2}$.

The spin of the electron was postulated to explain the existence of multiplets, or the fine structure of spectral lines. Using spectroscopes of very high resolving power, it is possible to show that spectral lines are made up of a number of very closely spaced lines. This is referred to as the hyperfine structure. To explain hyperfine structure it is necessary to introduce the conception of the nucleus spinning. The nuclear spin energy has a quantum number i associated with it. This matter, however, is beyond the scope of this book.

66. The Periodic Table.—The structure of the periodic table may be understood by considering how the electrons fill into the energy states defined by the four quantum numbers n , l , m and s . The electrons fill into the levels in order of increasing energy. In filling the various energy states the electrons obey the Pauli exclusion principle, which states that in any one atom there is never more than one electron with a given set of quantum numbers n , l , m and s . This limits the maximum number of electrons in an electron shell. The successive electron shells are called the K , L , M , N , O , P and Q shells for $n = 1, 2,$

3, 4, 5, 6 and 7. The K shell is nearest the nucleus, the others following in order of increasing n .

The lowest energy state is the $n = 1$ state. Here $l = 0$, $m = 0$ and s can be $-\frac{1}{2}$ or $+\frac{1}{2}$. According to the Pauli exclusion principle there can only be two electrons in this shell. Hydrogen with one electron, and helium with two electrons complete this, the $1s$ level. When two electrons of opposite spin occupy the same energy level as in helium the electrons are said to be paired. Helium has a $1s^2$ configuration, that is it has two electrons in the $1s$ level.

The $n = 1$ shell being filled, the electrons now start to occupy the $n = 2$ shell which is the shell of next lowest energy. For $n = 2$, $l = 0$ or $l = 1$. For $l = 0$, $m = 0$ and therefore only two electrons can be accommodated in the $2s$ level. Lithium has one and beryllium has two electrons in the $2s$ level. The configuration of beryllium is $1s^2 2s^2$. When $n = 2$, $l = 1$, m can equal 1, 0, or -1 , so there are three equivalent $2p$ energy states corresponding to the three m values. These three states can accommodate six electrons. Boron has two electrons in the $1s$, and two in the $2s$ shell so its fifth electron will enter the $2p$ level, say the $m = 0$ state, giving boron a $1s^2 2s^2 2p$ configuration. Carbon has two electrons in the $2p$ level. The second electron can enter either the $2p$ state which already contains an electron or it can enter one of the unoccupied $2p$ states. According to Hund's principle of maximum multiplicity, electrons remain unpaired as long as possible, so the second electron will enter a new $2p$ state. When nitrogen is reached the three $2p$ states each contain an electron; so with oxygen the fourth $2p$ electron must enter an occupied state and pair with an electron of opposite spin. The $2p$ level is completed by neon.

In the next period of eight elements from sodium to argon the electrons fill up the M shell entering the $3s$ and $3p$ levels in the usual manner. The next electron would now be expected to enter into the $3d$ level. However, the energy of the $4s$ level is lower than that of the $3d$ level so the electrons fill up the $4s$ level before the $3d$. This gives rise to the first transition series from scandium to zinc. In this series the outer electronic configuration is $4s^2$, and the electrons fill an inner shell, the $3d$ shell. These elements, called transition elements¹ resemble each other chemically and are said to show horizontal similarity.

The remainder of the periodic table is constructed by filling the higher levels. There is a second series of transition elements from yttrium to cadmium. In this series the $4d$ level does not fill until the

¹ The term transitional element was formerly applied to elements in Group VIII of the table, e.g., Fe, Co, and Ni. The term here is applied to the elements in which filling is taking place in a d level which is inside a completed s level. It should be noted also that the elements of Group VIII of the older type of table have now been divided between Groups VIII, IX and X. Groups IX and X contain only transitional and no normal elements. Group O of the older type of table is now called Group VIII (normal). For a more extensive account of the present classification see Whetler, *Chemistry and Industry*, 1947, p. 639.

5s shell has been completed. The third transition series is lanthanum, hafnium and thence to mercury.

The rare earth series the lanthanides, resembles the transition elements as filling of an inner shell by electrons also occurs. This series extends from cerium to lutecium and involves the filling of the 4f level which is inside an outer shell of $5s^2 5p^6 5d^1 6s^2$. Because the filling is deep in the atom, the lanthanides are very similar in properties and are very difficult to separate. It is believed that the elements thorium to californium may form a second rare earth series, the actinides. In this series filling of the 5f level takes place inside the configuration $6s^2 6p^6 6d^1 7s^2$.

The actual filling up of the levels is shown in Table XIX and a periodic table based on these ideas is shown in Chapter I.

67. The Dual Nature of Matter and Waves.—Although Bohr's theory is able to explain in a very satisfactory manner the periodicity running through the properties of the elements, the presence of transition groups in the Periodic System, and many other points connected with the nature of the atom, it fails to answer completely more complicated questions which arise.

For example, Bohr's quantum theory of the atom gives no explanation of the intensities of spectral lines unless further assumptions are made. Nor can it explain the more complicated spectra. Even the spectrum of helium, next in difficulty to that of hydrogen, cannot be adequately dealt with by the Bohr theory. Moreover, the arbitrary postulates on which it is based, running, as they do, completely counter to classical conceptions, are difficult to accept without explanation.

The system of wave-mechanics provides an explanation of the Bohr postulates, and at the same time extends the theory so that the more complicated problems of atomic structure can be effectively attacked.

Bohr's theory looks upon the electron as a material particle, but in 1924 de Broglie put forward the new idea that all moving material particles of whatever nature have wave-properties associated with them. These particles will, of course, include electrons. The fact that electrons can possess the properties both of particles and waves was suggested by the similar state of affairs existing with light. As is well known, Newton's view of the nature of light was that it was corpuscular.¹ His theory accounted satisfactorily for the laws of reflection and some other properties of light. In the nineteenth century, however, Young's experiments on interference and diffraction of light led to the view that light possessed the properties of waves, a theory put forward as early as

¹ Newton does, however, appear to have introduced a periodicity into his theory to explain, for example, Newton's rings. To this extent he may be said to have anticipated the particle-wave-motion theory.

1690 by Huygens, but discarded owing to the greater prestige of Newton. Young's work caused the complete destruction, for the time being, of the corpuscular theory, and it was shown that the wave theory could not only explain the newly discovered phenomena of interference, but also the laws of reflection and refraction in a manner just as satisfactory as the corpuscular theory. Early in the present century, however, new phenomena were discovered which the wave theory by itself could not explain. The photo-electric-effect for example demanded that light should be regarded as made up of photons, which possessed the properties of both corpuscles and waves. Photons were looked upon as "wave packets" or pulses, and were associated with energy proportional to the frequency of the wave—quanta, in fact, given by Planck's equation

$$E = h\nu.$$

The application of a similar conception to moving material particles is the basis of wave-mechanics. De Broglie supposed that the wavelength, λ , associated with a moving particle is given by

$$\lambda = h/mv,$$

where h is Planck's constant, m is the mass, and v the velocity of the moving particle.

If this is the case, it should be possible to calculate the wavelength associated with the electron when it is moving with a given velocity. When this calculation is carried out the wavelength associated with an electron which has acquired energy by falling through a potential difference of 100 volts is found to be 1.22 Å, which is of the order of the wavelength of soft X-rays.

If electrons are, in fact, associated with waves it would be expected that they would show the phenomena of interference and diffraction in the same way as light. This suggestion, which was made by Elsasser in 1925, was verified by Davisson and Germer, who showed experimentally that there was selective reflection of electrons at the surface of a nickel crystal. The results were very similar to those obtained with X-rays, and when the effective wavelengths of the electrons were calculated by the usual diffraction formula the values obtained agreed with those given by the de Broglie equation within the limits of experimental error. These experiments, and those of G. P. Thomson, are referred to again in § 139.

Perhaps the most outstanding experimental evidence that electrons are associated with waves is provided by the fact that it is possible to construct an electron microscope. It is well known that the resolving power of an optical microscope is limited by the wavelength of the light used, the size of the object which can be successfully seen varying with

the wavelength. The lowest wavelength that can be used with an optical microscope is in the neighbourhood of 3000 Å. Since electrons can be deflected by electric and magnetic fields it is possible to construct magnetic and electrostatic focusing systems and hence to use a beam of electrons in the same way as a beam of light. Of course, the electrons cannot be "seen" in the same way as light, but they can be photographed, like X-rays. The smallest object that can be "seen" with an optical microscope has a diameter of about 2×10^{-4} cm., but since electrons have a very much smaller effective wavelength, the electron microscope can be used to "see" objects of diameter as small as 10^{-6} cm., which is almost of molecular dimensions. With the aid of this instrument it has been possible to photograph macro-molecules, such as protein molecules. The disadvantage of the electron microscope lies in the fact that the beam of electrons may destroy, or damage the object being "viewed", particularly biological material.

It has thus been established experimentally that electrons have the properties of waves. At the same time they have the properties of particles, since they have mass and momentum, which can only be thought of as the attributes of corpuscles.

Not only is this true of the electron, but it also holds for atoms and molecules. Stern showed in 1932 that atomic and molecular beams were diffracted at crystal surfaces in the same way as electrons, so that we are forced to the conclusion that all matter has a wave aspect as well as a particle aspect. Thus both matter and electro-magnetic waves have a dual nature. Matter has a wave aspect, and waves have a particle aspect. The two are complementary. It can be shown that if an experiment is devised to test the wave-properties of matter, then the matter behaves entirely as waves. Conversely if an experiment is devised, say, to measure the momentum of a particle, then the material side of matter only will be in evidence. If we consider wavelength λ , as the property of waves we are thinking of, and momentum as the property of particles, the two are connected by the de Broglie equation

$$\lambda = \frac{h}{mv}$$

since mv is the momentum. Thus the connecting factor is h , Planck's constant.

The de Broglie equation can also be used to connect frequency ν

with ~~energy~~ ($\frac{1}{2}mv^2$) since the wavelength, $\lambda = \frac{v}{\nu}$. We thus have

$$\nu = \frac{mv^2}{h} = \frac{\frac{1}{2}mv^2}{\frac{h}{2}}$$

We see again that the factor connecting frequency (a wave property) with kinetic energy (a particle property) is Planck's constant, h .

68. Heisenberg Uncertainty Principle.—In an electron diffraction experiment a beam of electrons of uniform energy is allowed to impinge upon a crystal which acts as a diffraction grating. The diffracted beam then falls on a photographic plate. The pattern shown on the plate is an ordinary diffraction pattern; it consists of concentric light and dark rings. These correspond to places on the plate where many or few electrons have fallen. From the spacing between the light rings a wavelength corresponding to the electron beam can be calculated. The de Broglie relation then gives the momentum of the electrons. If a single electron could be passed through the grating the position on the plate to which it would go could not be predicted, but the positions where many electrons strike and also those to which few electrons go can be foretold. It is this tendency for electrons to strike some positions and not others which produces the diffraction pattern. In other words certain target positions are more likely; so that while the energy and the momentum of the electron beam are known, the points where the electrons strike the plate become matters of relative probability. There is no certainty that a particular electron will be found in a particular position on the plate but the intensity of the electrons at that point gives a measure of the probability of finding the electron at that spot. Heisenberg generalised considerations of this nature into a principle now called the Heisenberg Uncertainty Principle. This is one of the fundamental postulates of modern quantum physics. The Principle states that it is impossible to determine simultaneously the momentum (or energy, or velocity) and the position of a particle. Further, if Δx is the uncertainty in position, and Δp is the uncertainty in momentum, then $\Delta x \Delta p$ is approximately equal to Planck's constant, h . This means that the more accurately one quantity is determined the less accurately can the other be measured. The uncertainty arises from the fact that in carrying out a measurement the particle under observation interacts with the particles (e.g., photons) used in the measurement. The result of the principle is that the classical system of mechanics (which demands the simultaneous determination of position and momentum) cannot be applied to atomic particles. With macroscopic systems the Heisenberg uncertainty is negligible compared with experimental error, so the methods of classical mechanics can be applied to such systems with no appreciable error.

69. Wave Mechanics.—In order to consider the behaviour of atomic particles two new systems of mechanics, the Heisenberg matrix mechanics, and the Schroedinger wave mechanics have been devised. Though the two systems differ in form they are identical in content. The wave mechanical approach will be considered here.

The fundamental postulate of wave mechanics is that an equation of the type

$$\frac{\delta^2\psi}{\delta x^2} + \frac{\delta^2\psi}{\delta y^2} + \frac{\delta^2\psi}{\delta z^2} = \frac{-4\pi^2}{\lambda^2} \psi$$

may be applied to all particles—electrons, photons, and atoms. If the de Broglie relationship is added as a further postulate the right-hand side of the equation becomes $\frac{-4\pi^2 p^2 \psi}{h^2}$. The kinetic energy of a

particle is $\frac{p^2}{2m} = (E - V)$, where E is the total energy and V is the potential energy. So, substituting $2m(E - V)$ for p^2 and transferring the right-hand side to the other side of the equation we have

$$\frac{\delta^2\psi}{\delta x^2} + \frac{\delta^2\psi}{\delta y^2} + \frac{\delta^2\psi}{\delta z^2} + \frac{8\pi^2 m (E - V) \psi}{h^2} = 0$$

which is the wave equation of a single particle. This equation is usually called the Schroedinger equation. In considering a particular problem the values for m and V are substituted in the equation which is then solved for ψ and E . ψ is called the wave function. It has the physical significance that the value of ψ^2 for a particular particle at any point in space is proportional to the probability of finding the particle at that point. To find the actual probability ψ^2 must be multiplied by a constant N which is such that $N^2 \int \psi^2 d\psi$ taken over the whole of the space is equal to 1. This process is known as normalising the wave function.

In order that ψ can have a physical significance it is necessary to add a further postulate, viz., that the only significant solutions of the wave equation (known as eigenfunctions) are those which are single-valued, finite, and continuous over all space. This postulate is most important for it leads to the conclusion that there are only certain values of E (eigen-values) for which there exists a physically significant value of the energy. The concept of quantisation of energy, that is the restriction of the energy to a number of discrete values, arises from the solution of the wave equation. The concept is not introduced as a postulate as is done in the Bohr theory. The eigenfunction for an electron is called an atomic orbital by analogy with the classical electron orbits.

Wave mechanics may be applied to the problem of the hydrogen atom. Here the interest is in the behaviour of an electron outside a nucleus. Assuming the nucleus to be stationary, m is the mass of the electron, and V is $-\frac{e^2}{r}$. The Schroedinger equation can be solved fully and it is found that the value of ψ depends on three integral constants,

n , l , and m . The solution also shows that these numbers are related so that l is not greater than $n - 1$, and m has values from $-l$ to $+l$. The three quantum numbers and the relationships between them which arise from the solution of the wave equation are the same as those which are deduced from a study of spectra. (The spin of the electron does not come into the wave mechanical treatment; it must now be added.) The energy of the hydrogen atom deduced from the wave equation is $\frac{2\pi^2me^2}{n^2h^2}$ where n is 1, 2, 3, ... etc. This value of the energy is

the same as was obtained in the Bohr treatment; for the hydrogen atom the energies arrived at by both methods agree with experiment, but for more complicated atoms the wave mechanical treatment is superior. In these complex problems the exact solution of the wave equation becomes impossible, but approximate methods of solution are available.

70. Shapes of Atomic Orbitals.—Surfaces in space, within which, as it were, an electron will spend most of its time, can be drawn for the various states of the electron. The shape of a surface given by an atomic orbital depends mainly on the l quantum number. For $l = 0$,

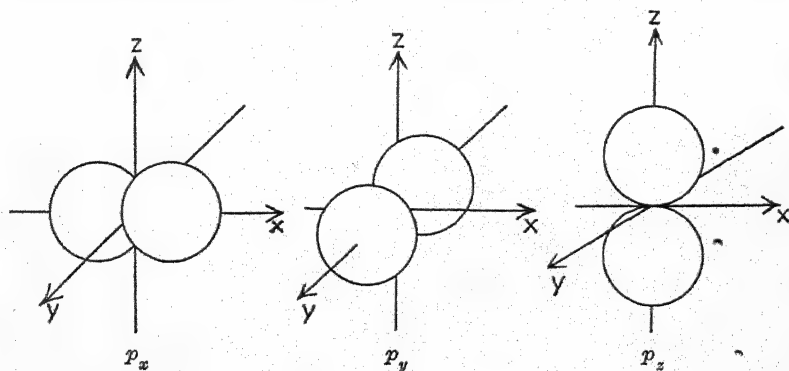


FIG. 41.— p Orbitals.

that is, an s state, the probability of finding an electron in any position depends only on the distance from the nucleus; the shape of the boundary surface is therefore a sphere. The boundary surfaces corresponding to a p state, $l = 1$, form three pairs of spheres of equal radius. The spheres comprising a pair touch at the nucleus, and the three lines obtained by joining the centres of each pair are at right angles (Fig. 41). This means that p electrons, for example the three $2p$ electrons of nitrogen, are confined so that each one is near one set of three rectangular axes. The bonds formed by such electrons will be directional in character. The three p electrons can be differentiated by the use of

the terms p_x , p_y , and p_z . The d surfaces, that is those for $l = 2$ are like the p orbitals in possessing directional properties. Some of the d orbitals are shown in Fig. 42. The importance of the directional properties of p and d orbitals will be seen in the discussion on the shapes of molecules in connection with the quantum theory of valency.

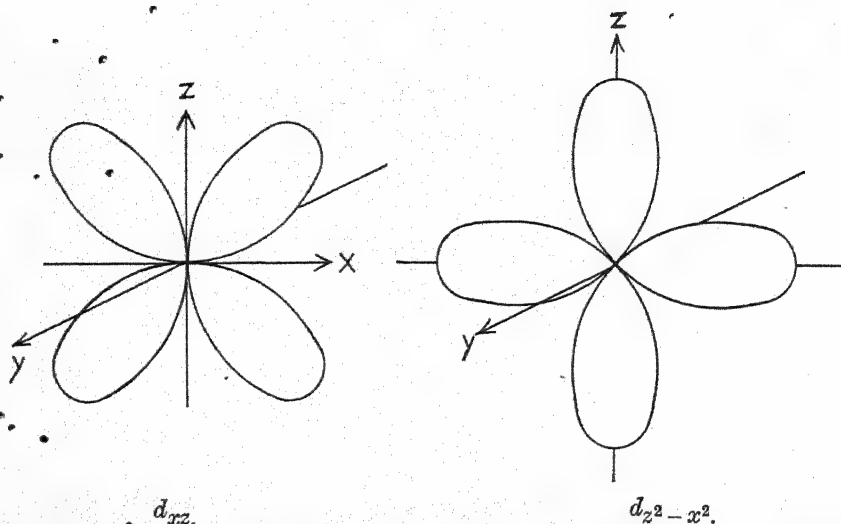


FIG. 42.— d Orbitals.

71. Ortho- and Para-Hydrogen.—The prediction that there should be two forms of hydrogen, which was made on the basis of wave-mechanics, is interesting, as it has been verified experimentally.

The nucleus of the atom is spinning, and when two hydrogen atoms come together to form a molecule, they may unite in such a way that the nuclear spins aid each other (symmetrical) or oppose each other (anti-symmetrical). In the first instance, ortho-hydrogen is produced, and in the latter, para-hydrogen. The ordinary gas consists of a mixture of the two forms in the proportion of about three parts of ortho to one part of para-hydrogen, at ordinary temperatures. The proportions of the two forms present vary with the temperature. Since the form with no resultant spin, i.e., the para-form, will have less energy than the other, the gas should consist mainly of this form at very low temperatures. This was tested by Bonhoeffer, who was able to prepare 99.7 per cent. pure para-hydrogen by cooling. In consequence of the difference in energy content, the two forms will possess different specific heats.

SUGGESTIONS FOR FURTHER READING

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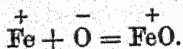
CHAPTER IV

VALENCY

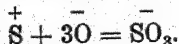
72. **Development of the Theory of Valency.**—Such radical changes have taken place in our views of the meaning of valency that it is advantageous to trace the development of the conception.

Like many other theories, the theory of valency arose from the application of the atomic theory to chemical reactions. The burning question at the beginning of the nineteenth century was the way in which atoms combined with each other. From a study of electrolysis, Davy, in 1807, came to the conclusion that opposite parts of the atom (defined according to the view of Dalton, which included atoms of both elements and compounds) possessed opposite electrical charges, produced by induction. His view does not seem to have been generally accepted, or to have been given serious thought. In 1812, Berzelius put forward an hypothesis which was considerably more comprehensive. He started with the assumption that each atom possessed a characteristic electrical polarity, which was concentrated in at least two poles, of different intensity and different sign. Only the resultant electric force mattered as regards external properties, so that although an atom might possess numerous different charges, it appeared to be unipolar. Compounds were formed by complete, or partial neutralisation of the opposite charges of other atoms. Thus, according to this view, all compounds were made up of two parts, electrically opposite in character, and the theory was therefore called the dualistic theory.

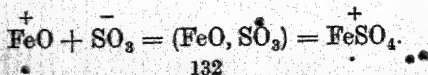
Thus the iron atom was supposed to have a positive charge, and the oxygen atom a negative one, and combination occurred by the partial neutralisation of these charges,



Similarly sulphur had a positive charge which was fairly large, and could take up three atoms of oxygen.



The FeO and the SO_3 thus produced were endowed with small residual charges, and could therefore partly neutralise each other and form another compound.



The FeSO_4 was still not quite neutral, for it could take up seven molecules of water to make the crystalline salt, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

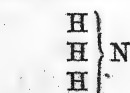
Some of the assumptions of this theory were soon threatened. Berzelius had taken oxygen as the most negative element, but the discovery of the properties of chlorine made this questionable. Again, the rising "organic chemistry" did not prove a suitable ground for dualism. At first, work in this branch of chemistry received ample explanation at the hands of dualism. Organic compounds were classed together as simple compounds in which groups of atoms, called compound radicals, played the part of elements, an assumption that was put on a firm footing by the work of Gay-Lussac on cyanogen. The radical was the electropositive part of the molecule, which could take up oxygen as the opposite pole. This, of course, naturally excluded the presence of oxygen in compound radicals, and Berzelius had to capitulate on this point when Liebig and Wöhler discovered the benzoyl radical ($\text{C}_6\text{H}_5\text{CO}$).

In 1839, Bunsen discovered the radical cacodyl, $\text{C}_4\text{H}_{12}\text{As}_2$. Research on this radical showed in a much clearer way than hitherto, how the atoms were combined in it. To this work Berzelius took such a one-sided attitude that he not only lost many of his adherents, but had to face severe attack from many quarters.

The discovery of substitution in organic compounds by Dumas was the final point. Dumas showed that the hydrogen in many compounds could be replaced by chlorine, without producing any very great change in the properties of the compound. This is well illustrated by the case of acetic acid. When one hydrogen atom of the methyl group is replaced by one of chlorine, monochloroacetic acid, $\text{CH}_2\text{Cl} \cdot \text{COOH}$, is formed. This substance resembles acetic acid quite closely, and yet the positive hydrogen has been replaced by the very negative chlorine. Facts like this were quite incompatible with dualism, and proved the downfall of the theory.

It may be mentioned in passing that in many respects our modern view of chemical combination resembles the dualistic theory, as will be seen later.

To take the place of the dualistic theory, Dumas proposed a theory of types. This held that the chemical nature of a compound depended primarily on the arrangement and number of its constituent atoms, and that the chemical nature of the atoms was of lesser importance. This theory had advantages, and was improved by Gerhardt in 1856. There were four types on which organic compounds could be classified. These were:—



1. Ammonia Type.



2. Water Type.



3. Hydrogen Type.

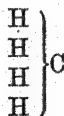


4. Hydrochloric Acid Type.

Organic compounds were all made by substituting elements or radicals for the hydrogen. Thus, acetamide was of the ammonia type, and was obtained from it by substitution of the acetyl group, C_2H_3O , for one atom of hydrogen. Methyl alcohol was of the water type, since methyl alcohol could theoretically be obtained from water by substitution of a methyl radical for an atom of hydrogen. From these four types, Gerhardt was able, in a most ingenious way, to explain the nature of nearly all the known organic compounds. These views were generally accepted, and the number of types was extended by Williamson and Kekulé. Williamson introduced mixed types, which were derived from two or more of the four types previously mentioned. Thus, benzene-sulphonic acid belonged to the mixed type

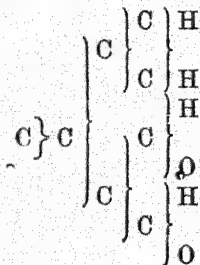


Kekulé introduced the new type—



which represented methane.

In spite of the existence of these types there was frequently some uncertainty about the type to which a compound belonged, and the accumulation of a large number of types in a complex substance caused confusion. To give an example of the complexity of the explanation, the formula of the radical of phthalic acid may be quoted. This was given as



Before the Gerhardt theory of types had reached the apex of its development, a new point of view was slowly forming. Frankland, in 1852, having studied some organo-metallic compounds, came to the conclusion that the regularities noticed in the composition of organic and inorganic compounds were due to the fundamental properties of the atoms

contained in them. The regularities were due to a *saturation capacity*, which was characteristic of the element, and which could grow within certain limits. The saturation capacity of an element was the number of atoms of another element or radical which could combine with one atom of the original element, to form a compound. For the elements of the nitrogen group, for example, it was three or five. In Frankland's own words: "When the formulæ of inorganic chemical compounds are considered, even the superficial observer is struck with the general symmetry of their constitution; the compounds of nitrogen, phosphorus, antimony, and arsenic especially exhibit the tendency of these elements to form compounds containing three or five equivalents of other elements, and it is in these proportions that their affinities are best satisfied; thus, in the ternary group, we have NO_3 , NH_3 , NI_3 , NS_3 , PO_3 , PH_3 , PCl_3 , SbO_3 , SbH_3 , SbCl_3 , AsO_3 , AsH_3 , AsCl_3 , etc., and in the five atom group, NO_5 , NH_4O , NH_4I , PO_5 , PH_4I , etc. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms." In this way the fundamental basis of the theory of valency was laid.

The two organic chemists Kolbe and Kekulé took up the idea, and the latter arrived at the conception of the quadrivalency of carbon. Numerous difficulties, however, soon arose. The first question was whether valency was to be regarded as constant, or whether, under certain circumstances, it could vary. Frankland, as has already been stated, believed that it could vary within certain limits, and he was supported in this view by Kolbe. Kekulé, however, defined valency as a fundamental, and strictly invariable property of the atom. However, the fact that valency, or saturation capacity did change, was evident from the existence of such substances as phosphorus trichloride and pentachloride. Both of these are definite compounds, and yet one contains more chlorine than the other. To explain this, Kekulé introduced the system of molecular and atomistic compounds. In atomistic compounds, the elements had their full saturation capacity satisfied. Thus, common salt would be an atomistic compound, because one atom of sodium has combined with one atom of chlorine to make a molecule of sodium chloride, and the valency of the sodium is satisfied. Molecular compounds were made by the combination of two atomistic compounds, in virtue of the forces of affinity. The molecular compounds were supposed to be less stable than the atomistic compounds. Phosphorus trichloride was supposed to be an atomistic compound. The saturation capacity of the phosphorus had been satisfied by three atoms of chlorine. We should say the valency of phosphorus is three. Phos-

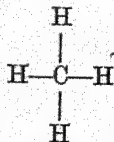
phorus trichloride, however, can combine with a molecule of chlorine to form phosphorus pentachloride, which, according to Kekulé, was a molecular compound. The valency of phosphorus must still be regarded as three. Phosphorus pentachloride could be written $[\text{PCl}_3]\text{Cl}_2$, to emphasise this. Moreover, phosphorus pentachloride, on heating, dissociates into phosphorus trichloride and chlorine, and thus it gives all the appearances of being a molecular compound, being less stable than the trichloride, which is atomistic.

However, certain substances, which, according to Kekulé, should be regarded as molecular compounds, were markedly stable. Particularly was this so with phosphorus pentafluoride. The existence of this stable compound convinced many that valency was variable, and militated against Kekulé's theory. Erlenmeyer supposed that each atom had a higher valency limit which need not always be satisfied. In determining valency, the fully saturated compounds only should be considered.

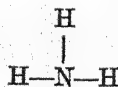
The generally accepted view of valency at this time may be summed up as follows: Every element possesses the power to combine with other elements, but the extent to which this combination can go on is limited. Every element has a saturation capacity. In order to give a definition of saturation capacity, or valency, it may be said that valency is the number of atoms of hydrogen with which one atom of the element will combine. Thus, the valency of oxygen is two, because two atoms of hydrogen, combine with one atom of oxygen to form water. The valency of nitrogen is three, because one atom of nitrogen will combine with three atoms of hydrogen to form ammonia, NH_3 . Looked at from this point of view, it was natural to assume that atoms possessed valency "bonds", which might be pictured as solid rods extending from the atom. Each "bond" was able to attach itself to one hydrogen atom, which possessed one "bond". Combination, therefore, meant the fusion of these "bonds".



Water.
Oxygen has
two "bonds";
it is bivalent.



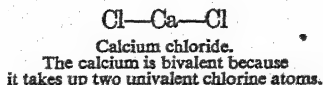
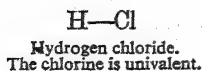
Methane.
Carbon has
four "bonds";
it is quadri-
valent.



Ammonia.
Nitrogen has
three
"bonds"; it is
trivalent.

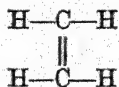
The conception of valency "bonds" made it easier to elucidate chemical combination between elements when one of them was not hydrogen. Many metals would not combine with hydrogen, and so their

valencies could not be determined directly according to the above plan. They would, however, combine with chlorine, which was known to be a univalent element, because one atom of chlorine combined with one atom of hydrogen to give one molecule of hydrogen chloride. The valency of the metals could thus be determined through the chloride.



Such a view of valency "bonds" would naturally tend to give the idea that valency was a directed force, manifested at certain points in the atom. Erlenmeyer held that this was so, and this view led to the hypothesis put forward by van't Hoff, and almost simultaneously by Le Bel, of space-directed valency forces giving rise in the case of carbon to a tetrahedral model, which, in actual fact, had been suggested by Wollaston some ten years before. The theory of stereochemistry has been of outstanding importance in organic chemistry in explaining the existence of isomers and the phenomenon of optical activity.

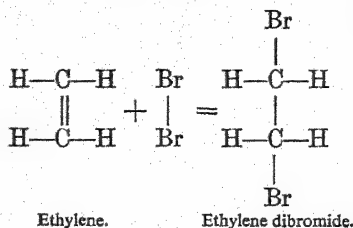
Whilst in inorganic chemistry the assumption of variable valency was a necessity, in organic chemistry this was not so, and for a long time the only exception to the quadrivalent carbon atom was found in carbon monoxide, CO. To make carbon always quadrivalent, the theory of double and triple bonds, or unsaturation was suggested. Thus, in ethylene, C_2H_4 , it was supposed that the two carbon atoms were linked by two bonds, instead of one,



The bond between the two carbon atoms was called a "double" bond. In acetylene, C_2H_2 , it was necessary to suppose that the two carbon atoms were joined by a "triple" bond.

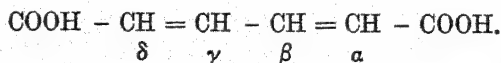


In both cases the quadrivalency of carbon is maintained. Substances containing these double and triple bonds are said to be "unsaturated". They possess much greater chemical activity than substances containing single bonds only ("saturated" substances), and readily enter into "addition" reactions, whereby they become saturated. In these reactions, elements or groups are added to the unsaturated molecule without the elimination of any atom. Bromine, for instance, adds on to ethylene, giving ethylene dibromide.

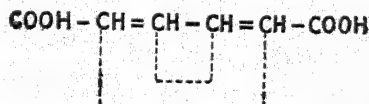


The explanation of the additive powers of unsaturated bodies was given in a satisfactory way by Thiele, who supposed that in the formation of the double bond the affinity force is not completely satisfied, so that part of the valency is left. To this fraction Thiele gave the name "partial valency". These partial valencies were capable of adding on the usual addition elements or groups.

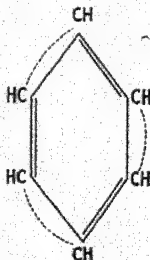
This theory explained in a remarkably neat way the mode of addition of elements to a conjugated system of double bonds, *i.e.*, an alternation of double and single bonds, as found in muconic acid, for example.



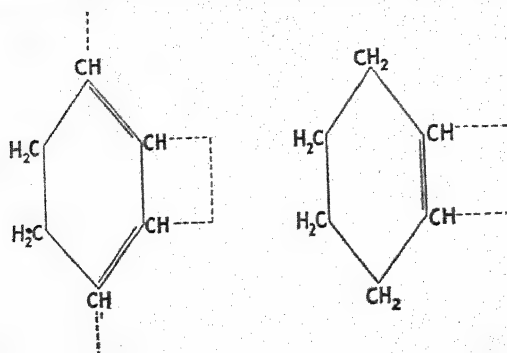
The partial valencies of the β - and γ -CH groups were supposed to satisfy each other, thus:—



This explains the fact that addition to muconic acid always results in the formation of an α - δ -compound. The theory also explains the relative inactivity of benzene, although this substance contains three double bonds. These double bonds form a conjugated system, and so in the end the molecule behaves as if it were saturated.



It also explains the aliphatic nature of the partly hydrogenated ring:—



A consideration of valency in the light of the Periodic Table showed that in the compounds of elements with oxygen, assuming the valency of oxygen to be 2, the valency ascended regularly from Group I to VII.

Thus, taking the elements in the first short series in order, Table XX. shows the compounds formed with hydrogen, and with oxygen.

TABLE XX.—VALENCY AND THE PERIODIC TABLE.

	O. He	I. Li	II. Be	III. B	IV. C	V. N	VI. O	VII. F
Formulae of Hydrogen Compounds.	—	LiH	BeX ₂ **	B ₂ H ₆ * B ₄ H ₁₀	CH ₄	NH ₃	OH ₂	FH
Formulae of Oxygen Compounds.	—	Li ₂ O	BeO	B ₂ O ₃	CO ₂	N ₂ O ₅	— (SO ₃)	F ₂ O* (Mn ₂ O ₇)

* Anomalous.

** Be does not form a hydride, but combines with two atoms of a univalent radical such as (CH₃).

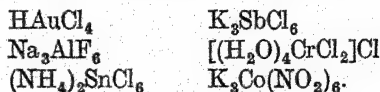
There were, however, numerous exceptions when other compounds than those with oxygen were considered. Blomstrand pointed out that it was better to take hydrogen compounds. From this point of view, it follows that the valency of an element depends on the nature of the element with which it is compounded. Blomstrand thought this difference to be due to the electrochemical nature of the combining element. He pointed out that a strongly electro-positive or electro-negative element, exerting all its force, always took on the lowest valency. To a certain extent, then, he returned to the view of Berzelius.

Owing to the connection between affinity and valency, many investigators tried to find an explanation of the former in the hope that it might lead to an elucidation of the latter. However, the view that there was any force behind valency dropped out, and Lothar Meyer summed up the views of the time (1870) by the statement that "By chemical

valency we mean the ratio of the atomic weight to the equivalent weight of an element. Valency is thus a pure number". (See Chapter I., § 11.) It is clear, then, that he did not look upon it as any expression of force.

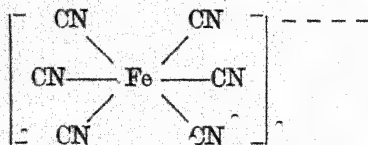
The existence of molecular compounds was still not satisfactorily explained. These compounds included: (1) the so-called double halides, such as the stannichlorides, platinichlorides, silicofluorides, etc.; (2) the complex cyanides (such as ferro- and ferri-cyanides), and nitrites (such as cobaltinitrites); (3) the hydrates; (4) the ammines, complex compounds containing ammonia; and (5) oxonium and sulphonium compounds, etc. (organic compounds of quadrivalent oxygen and sulphur).

The formulæ of some of these compounds are given below:—

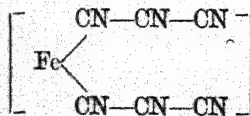


These compounds all appear to be made up of two molecules, each of which is capable of a separate existence. Thus, potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, may be regarded as compounded of 4KCN and $\text{Fe}(\text{CN})_2$. The formula could not, however, be written $4\text{KCN}, \text{Fe}(\text{CN})_2$, as this denotes that on solution in water, potassium, ferrous and cyanide ions would be produced, whereas actually, only potassium K^+ , and ferrocyanide $\text{Fe}(\text{CN})_6^{4-}$ ions are produced. Ions, such as the ferrocyanide, ferriocyanide, cobaltinitrite, etc., ions, are called complex ions.

The problem is to find some method of writing the formulæ of these complex ions in order to indicate their structure. Consider again the ferrocyanide ion, $\text{Fe}(\text{CN})_6^{4-}$. The six cyanide groups are here identical in their relationship to the iron atom, for they may be replaced by other groups, and no matter which one is replaced, the same compound results. They must be either linked to the central iron atom, giving the latter an apparent valency of six,



or they must be linked to each other in some such way as that illustrated below:—



Of these, the first assumption is preferable, since the second is incom-

patible with the statement made above that all six (CN) groups are equivalent as regards replacement.

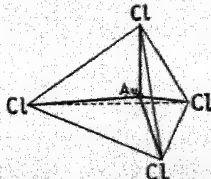
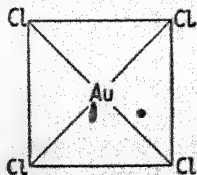
The consideration of a greater number of compounds of this type reveals the fact that the central atom of the complex ion frequently shows a maximum valency of six, though for some elements it may be four. The maximum valency appears to vary with the position of the element in the Periodic Table, as shown in the following Table.

TABLE XXI

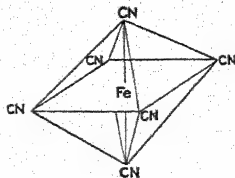
	Maximum Valency.
Hydrogen	2
Lithium—Fluorine	4
Sodium—Bromine	6
Rubidium—Uranium	(rarely 8)

Alfred Werner, in 1891 and the following years, propounded a theory which was capable of explaining the behaviour of these molecular compounds. According to this theory, there was a tendency amongst certain atoms to attach to themselves a definite number of other atoms or groups, irrespective of their valency. The maximum number of groups that could be added was called the *co-ordination number*. It is usually four, or six. The atoms or groups thus attached were supposed to be in the first zone. Besides these, the molecule could contain other atoms or groups which were in a second or outer zone. These were not so firmly held, and could be ionised in water, whereas those in the first or inner zone could not. To return to the example of potassium ferrocyanide; according to Werner, the substance could be written $K_4[Fe(CN)_6]$. The co-ordination number of the iron is 6, because the iron atom is surrounded by six cyanogen groups. These are in the first zone, and not dissociable. The whole group, $[Fe(CN)_6]$, or co-ordination complex (as it is called), can take up four potassium atoms, and these are in the second zone, and can be ionised in aqueous solution.

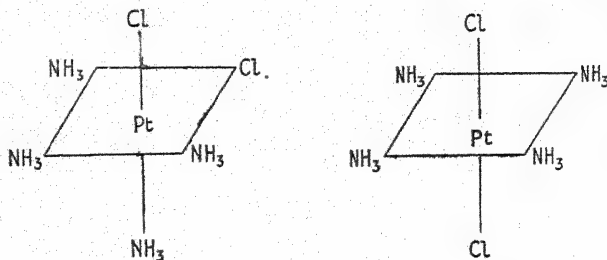
The spatial arrangement of these atoms and groups in the co-ordination compounds was also elucidated by Werner. The 4-co-ordinated compounds could have a planar or a tetrahedral structure.



The 6-co-ordinated compounds must be octahedral.

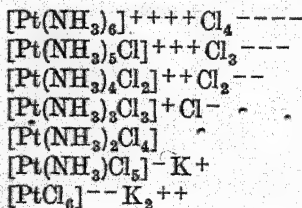


This was verified by the fact that there are two isomers of compounds of the type $[A_2MB_4]$, such as $[Pt(NH_3)_4Cl_2]$, which differ considerably in colour, crystalline form and other properties. On the octahedral theory they may be represented as



No other structure (plane hexagon, or prism are possible alternatives) would give this.

The electrical charges on the parts of these complexes were investigated by Werner. If, in the complex ion, a neutral molecule or group (e.g., ammonia, NH_3) is replaced by a negative ion (e.g., Cl^-), the charge on the complex ion is increased by one negative unit. Thus, if the complex is already positively charged to the extent of four units, it will be positively charged to the extent of three after the replacement. The following series of compounds may be prepared:—



The successive replacement of the neutral ammonia molecule by the electro-negative Cl^- decreases the charge on the complex ion, until the neutral compound $[Pt(NH_3)_2Cl_4]$ is reached, which does not ionise at all. Further introduction of Cl^- , and removal of NH_3 , makes the whole complex ion electro-negative, and it is possible for it now to combine with an electro-positive metal like potassium.

The view that the central atom can take up a *number* of groups irrespective of their valency was quite foreign to the conception of valency held at the time (1890-1900), and the theory met with a poor reception. More recently, however, it has been shown to be essentially accurate, and the co-ordination compounds have received satisfactory explanation on the electronic theory of valency (§ 75).¹

An important piece of work was that of Abegg in 1904, who returned to the idea that different valencies could be exhibited by an element, depending upon the element with which it was combined. He found that many elements had two kinds of valency which he called normal and contra-valency, and the sum of these was always eight. He called the maximum normal valencies positive for metals, and negative for non-metals. The contra-valency is of opposite polarity, and is much less frequently in evidence than the normal valency. The variation of these valencies with the group in the Periodic Table is shown in the Table below:—

TABLE XXII

Group in the Periodic Table.

		1	2	3	4	5	6	7	8
Maximum	Normal	+1	+2	+3	+4	-3	-2	-1	0
	Contra	(-7)	(-6)	(-5)	+4	+5	+6	+7	+8

All these valencies are not always exerted. Thus chlorine is usually univalent, for example, in hydrogen chloride, but in chlorine heptoxide, Cl_2O_7 , it is heptavalent, and is here exerting its maximum contra-valency.

73. **The Electronic Theory of Valency.**—With the advent of a more complete knowledge of the structure of the atom, the development of which has been outlined in Chapter II., came a much fuller idea of the meaning of valency. The old conception of valency as a number was gradually dropped, and attempts were made to find, in the modern theory of the structure of the atom, the reason for chemical combination. Valency is now regarded predominantly as a force, and not as a number.

The electronic theory of valency owes its rise to the recognition of the existence of electrons in the atom. It was very soon suggested that electrons themselves were in some way responsible for chemical combination, and J. J. Thomson (1904) stated, as a pure speculation, that chemical combination was the result of a transfer of an electron from one atom to another.

In 1904, Drude, as a result of studying Abegg's "rule of eight", already mentioned, actually stated that "Abegg's positive valency

¹ For an account of the preparation and properties of co-ordination compounds, see Ephraim, "Inorganic Chemistry" (Gurney & Jackson); a short account is given in "Inorganic and Theoretical Chemistry", Sherwood Taylor (Heinemann).

number, v , whether it is a normal or contra-valency, signifies the number of loosely attached negative electrons in the atom: his negative valency number v' means that the atom has the power of removing v' negative electrons from other atoms, or at least of attaching them more firmly to itself".

In spite of the fact that the views then held on the structure of the atom differed considerably from those held at the present time, Drude came very near to our modern ideas.

It was necessary to wait for the full development of the idea of the nuclear atom before any advance could be made in the electronic theory of valency. In particular was it necessary to arrive at the concept of the atomic number (§ 37), which was done in 1913. This gave the number of electrons in each atom, and provided something to work upon in connection with valency.

Further developments came from two independent sources. Both Kossel and G. N. Lewis noted that the element which immediately precedes an inert gas in the Periodic Table is always strongly electro-negative and univalent. Thus chlorine immediately precedes argon, fluorine precedes neon, bromine precedes krypton, and iodine xenon. All these halogens are univalent and strongly electro-negative. Immediately following the inert gases, on the other hand, are always strongly electro-positive elements, and again they are univalent. They are, in fact, the alkali metals. These elements and the corresponding atomic numbers are shown in the Table below.

TABLE XXIII.—TABLE SHOWING ELEMENTS IN THE NEIGHBOURHOOD OF THE INERT GASES

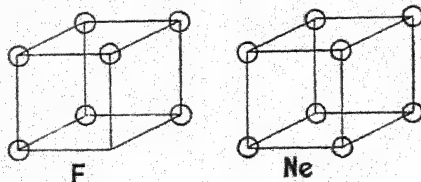
Group VII.	Group 0.	Group I.
F (19.0)	Ne (20.2)	Na (22.997)
9	10	11
Cl (35.457)	A (39.91)	K (39.096)
17	18	19
Br (79.916)	Kr (82.92)	Rb (85.44)
35	36	37
I (126.932)	Xe (130.2)	Cs (132.81)
53	54	55

The fact that the inert gases are extraordinarily stable suggests that they contain a stable configuration of electrons. It is clear from the atomic numbers (Table XXIII) that the halogens could all gain this stable configuration if they could take up one electron, and the alkali

metals could attain the same objective by giving up one electron. When the atoms reach the stable configuration in this way they become the corresponding ions. Thus, potassium, when it loses one electron, will have a resultant unit positive charge, and will, in fact, be the potassium ion, K^+ (§ 18). Fluorine, by gaining one electron, attains one negative charge, and becomes the fluorine ion, F^- . Extending this to the adjacent groups of the Periodic Table, calcium could give up two electrons and attain the stable argon configuration; sulphur in Group VI. could take up two electrons and also attain the stable argon configuration. The ions Ca^{++} and S^{--} would thus be produced. The valency of the element is obviously the number of electrons which the atom must give up, or take up, in order to attain a stable configuration. The electrons thus transferred are usually those in the outermost orbit, and are called *valency electrons*.

No atomic model whatever is involved in these statements. The only assumptions are that there are electrons in the atom; that each atom differs from the one preceding or following it in the Periodic Table by one electron, and that some of these electrons are held more firmly than others.

When Lewis and Kossel put forward their theories, they assumed a static model for the atom. They looked upon the electrons as at rest, and stated that the stable configuration of eight was produced when the electrons occupied the corners of a cube. It is now known, however, that the electrons are in motion in certain orbits (§ 66), and that the inert gases, which have stable configurations, have eight electrons in their

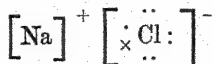


outermost energy level. Thus, the atomic constitutions of the inert gases are:—

Helium	2
Neon	2, 8
Argon	2, 8, 8
Krypton	2, 8, 18, 8
Xenon	2, 8, 18, 18, 8
Radon	2, 8, 18, 32, 18, 8

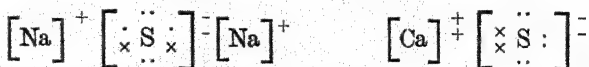
In every instance (except helium) the outermost level contains eight electrons (an octet), and this must be the number necessary to confer complete stability upon the atom. The other elements seek to attain

these configurations by taking up electrons from other atoms that will part with them. Thus, in the formation of sodium chloride, the sodium atom, which has one electron more than the number required for the stable neon configuration (its structure being 2, 8, 1), gives up this extra electron to chlorine, which has the structure 2, 8, 7, and could take it up to make the stable argon configuration. The electron is thus transferred from one atom to the other. This is represented as follows:—



The dots represent the electrons of the outermost level, these being (as a rule) the only ones which play any part in deciding chemical combination. The cross represents the electron transferred from the sodium atom.

In the formation of a salt, such as sodium sulphide, which contains a divalent radical, the sulphur requires two electrons to reach the stable configuration. It can get these by combining with two sodium atoms, which will each supply one, or by combining with one calcium atom, which has two available electrons in the outermost level.



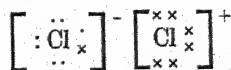
When such a salt is dissolved in water, the attraction between the constituent parts is decreased, and two ions are produced. Thus, sodium chloride gives sodium and chlorine ions. These ions are merely the original atoms which have reached the state of stability by gaining or losing electrons. The electrons lost or gained give them their charge. Thus



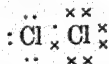
The bond between the component ions of a metallic salt in which electrons have been *transferred* from one atom to another is called the *electrovalent* bond. Sometimes it is called a *polar* bond, but it is preferable not to use this term. The compounds are called *electrovalent* compounds.

Two types of crystal structure are indicated by X-ray analysis (§ 134); one is typical of ionised compounds, in which the ions are closely packed in the crystal lattice, and the other is a neutral structure, much more open, found in substances like benzene, and ice. The X-ray examination of a substance like potassium chloride indicates that whilst the units in the space lattice are ions, the electrons are displaced from their orbits. In a certain measure a return to the dualism of Berzelius has been made in the conception of the electrovalent bond. More will be said about it later.

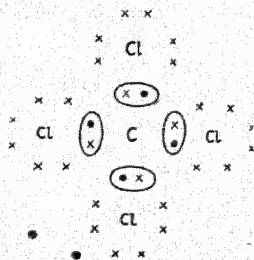
74. Covalent Linkages.—In organic, and in some inorganic substances, the linkage is not an electrovalent bond, for there will not be enough electrons to enable transference to be made. Thus, it is clear that in some compounds, such as the chlorine molecule, transference of electrons cannot have taken place. The transference of an electron from one of the chlorine atoms to the other (each having seven to start with) would allow one to attain the stable configuration, but would leave the other with six only.



Compounds of this type, too, are quite different from those that we have previously considered. They do not ionise, and as a rule they are much more volatile. To overcome the difficulty, it was supposed by Lewis that there was *sharing* of two electrons between the two atoms. In this way both could attain the stable structure.



Let us take another example. Carbon tetrachloride is obviously not similar to a metallic halide. It does not ionise, it does not dissolve in water, it is easily volatile. This is due to the fact that in this compound there are no unshared electrons involved in the bonding, and only a small residual electric field. The electronic structure of this compound is given below. The electrons belonging to the chlorine are represented by crosses, and those to the carbon by dots, and the shared electrons are enclosed in rings.



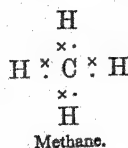
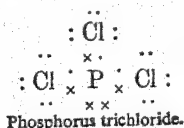
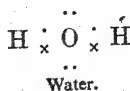
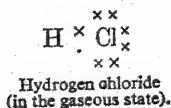
It will be seen that all the atoms have their full number of eight electrons, but they have only attained them by sharing electrons with other atoms.

A bond of this type, where one atom contributes one and the other also contributes one electron, is called a *covalent linkage*, or sometimes a *non-polar linkage*, although this term is one to be avoided.

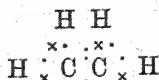
Covalent bonds hold the atoms together by the shared electrons. In the case of the electrovalent bond, the ions are held together only by electrostatic forces. The electron has been given up, and except for

the interaction of the electric fields, the two ions are free. According to Heitler and London, the formation of a covalent bond depends upon the resultant spin quantum numbers of the atoms (§ 80). The sharing of electrons is, in effect, a neutralisation or coupling of the electron spins in the two atoms.

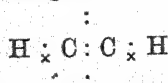
A few examples of substances formed by sharing electrons are given below:—



The double bond may be represented as the sharing of four electrons, as in ethylene



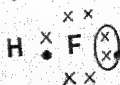
and the triple bond by the sharing of six, as in acetylene:—



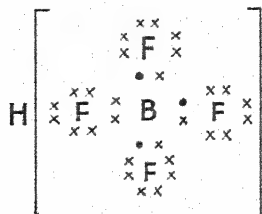
75. Co-ordinate Valency or the Semi-polar Bond.—Let us now consider what happens in the formation of such a compound as hydrofluoboric acid, HBF_4 . This is made as a result of the combination of hydrogen fluoride, HF , with boron trifluoride, BF_3 . On the electronic theory, boron trifluoride would be



It is seen that the boron can still take up two electrons to make its stable ring of eight. The fluorine atoms are satisfied, but the boron is still unsatisfied. Now, hydrogen fluoride is



and if it were permitted to share with the boron atom the two electrons enclosed in a ring, the latter would complete its octet. This is what is supposed to happen. The molecule

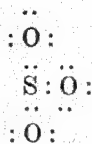


is thus formed; the hydrogen ionises off, and the radical BF_4 may be enclosed in brackets. The hydrogen has lost its original electron, and so is charged positively, whilst the BF_4 ion, as a whole, has gained it, and therefore becomes charged negatively.

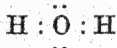
This type of bond is different from any so far considered, for it involves the sharing of two electrons which have both been supplied by the same atom. Since this process gives a satisfactory explanation of the co-ordination compounds of Werner, the bond has been called the co-ordinate bond, or the semi-polar bond, the latter being a term proposed by Lowry, since there is transference, and at the same time sharing. To save time in writing, the co-ordinate bond is frequently written $\text{A} \longrightarrow \text{B}$, or $\text{A} \rightarrow \text{B}$. Hydrofluoboric acid is $\text{HF} \rightarrow \text{BF}_3$.

This may now be applied to other examples. It is interesting to see how it is that the radical XO_4 occurs so frequently in inorganic compounds, X being Cl, Mn, Cr, S, Se, Te P, Si, etc. Let us take the formation of sulphuric acid from sulphur trioxide and water:—

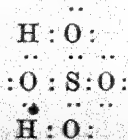
Sulphur trioxide is



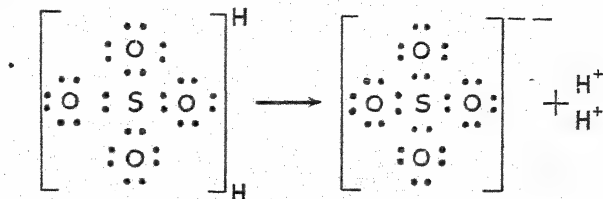
Water is



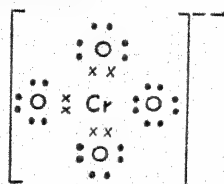
When the two come together we have



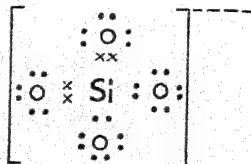
The hydrogen ionises off, and so we may write the $[\text{SO}_4]$ radical in square brackets, and the hydrogens outside¹. When the acid is dissolved in water the hydrogen ions are split off, leaving the radical with a double negative charge:—



The $(\text{CrO}_4)^{--}$ ion is, similarly,



The $(\text{SiO}_4)^{--}$ ion is



In every case, the octet of the central atom, X, of the ion (XO_4) is complete and fully shared. This is the reason for the stability of these ions. It also explains the comparative rarity of ions of the type (XO_5) and (XO_6) . Periodic acid, H_5IO_6 , is one of the few instances of a compound containing the (XO_6) ion.

The formation of salt hydrates, or the hydration of ions, is another example of co-ordination.

Lewis gave the name "acceptor" to any substance that could take up electrons to make its ring complete. Atoms which could supply them were called "donors".

76. The Electrovalent Bond and Ionisation.—The distinction between a metal and a non-metal now becomes more clear. A substance is a metal, or shows metallic properties, when it can form positive ions, and hence when it can lose its valency electrons. A substance is a non-

¹ The structure of H_2SO_4 is not necessarily as shown. It is written in this way for convenience in showing the SO_4 group.

metal when it tends to take up electrons. It is for this reason that hydrogen shows both metallic and non-metallic properties. It travels to the cathode in electrolysis of acids, and takes the place of a metal in them, because it has given up its one electron. On the other hand, it can form hydrides, such as lithium hydride, LiH , which on electrolysis gives hydrogen at the anode. In LiH the hydrogen has taken up an electron to form the stable helium configuration, and is therefore acting as a non-metal. The fact that elements on the right-hand side of the Periodic Table are predominantly non-metallic (*e.g.*, oxygen, chlorine, sulphur, nitrogen, phosphorus, etc.), is explained because here the elements tend to take up electrons to attain the stable configuration of the next inert gas. The atoms of elements towards the left of the Table tend to give up electrons and attain the stable arrangement of the inert gas next before, and are therefore metallic in character (*e.g.*, sodium, aluminium, magnesium, calcium, etc.). A certain number of elements do not form ionisable compounds, or only do so with difficulty. These elements are in the middle of the Table. The best example is carbon. We may analyse into two factors the ease with which metals form ions. The first is the number of valency electrons. The higher the valency, the more difficult it will be to remove further electrons, after the first electron has been removed. In an ion, there is the same nucleus as in the neutral atom, but fewer planetary electrons. Thus, as an electron is removed, the positive charge on the nucleus, which is unaltered by this process, has now a greater attractive effect on the remaining electrons. The more electrons are removed, the more firmly are the remainder held. Thus it becomes increasingly difficult to remove the electrons in polyvalent atoms.

The second factor is the atomic volume, which is governed by the size of the orbit of the valency electron. This will be further discussed in § 78.

77. **Transition Elements.**—The question of the valency of the transition elements is interesting, because these elements can exhibit variable valency. The valencies of some of the members of the first transition series are shown in the following table:

TABLE XXIV

Element.	Valencies.				
Titanium	2	3	4		
Vanadium	2	3	4	5	
Manganese	2	3	4	6	7
Iron	2	3			
Copper	1	2			

Raj Ballabh Singh
B.Sc. Final
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The variable valency arises from the electronic structure of these elements, which, as explained in the last Chapter (§ 66) involves the filling of a d shell inside a completed s shell.

Iron may be considered as an example. The outer configuration of the iron atom is $3d^6 4s^2$. When the two $4s$ electrons are lost a ferrous ion results; when a d electron is also lost a ferric ion is formed.

Another interesting point connected with the filling of an inner shell is the colour of the ions. All the elements from titanium to copper in the above series have coloured ions. If an ion is coloured it means that it absorbs light in the visible spectrum. If this is the case, transitions must take place in the atom which correspond to the absorption of quanta of visible light, of which the energy is between about 40,000 and 70,000 gram-calories per gram atom. In the case of an ion with a completed ring, such as Ca^{++} (of which the structure is 2, 8, 8) or K^+ (of which the structure is again 2, 8, 8), the only transitions that can take place are those to a higher orbit. The amount of energy required for this would be considerably greater than 70,000 gram-calories per gram atom. Consequently these ions absorb in the ultra-violet (corresponding to a large quantum), and appear to be colourless. In the case of an ion, or atom, with an incomplete ring, *e.g.*, sodium in the molecular form (of which the structure is 2, 8, 1, wanting 7 to complete the 8 of the third orbit), it is possible for the odd electrons in the incomplete outer ring to undergo transitions in the same energy level, *e.g.*, from $3p$ to $3d$, and the atom can thus absorb in the visible region. The vapour of sodium actually absorbs in the yellow. The sodium ion would have a completed outer ring (2, 8), and consequently transitions would have to occur from 2 to 3, involving a good deal of energy, and therefore absorption in the ultra-violet. In general, then, those atoms and ions will be coloured which have incomplete outer rings. We have this in the group of transition elements we have been considering. When ionised, the atoms still possess an incomplete third ring. Thus, the cupric ion is blue. Here the structure is 2, 8, 17. Transitions, involving small amounts of energy, can therefore take place in the third orbit itself. The cuprous ion, however, is colourless. Its structure is 2, 8, 18. The third group is complete, and transitions can only take place to higher quantum-groups involving the absorption of large amounts of energy.

The magnetism of the ions of this group is also bound up with the existence of incomplete rings. The ions of the elements from scandium to copper are all paramagnetic (*i.e.*, bodies containing these ions tend to set themselves parallel to the lines of force of the magnetic field; ferromagnetism is a special case of paramagnetism. Diamagnetic bodies tend to set themselves perpendicular to the field). It is known that ions with completed groups are diamagnetic; this may be due to a balancing of the magnetic moments of the orbits. Ions with incomplete groups are paramagnetic, as the magnetic moments are unbalanced.

The valencies of certain non-transition elements, particularly the elements of Groups III., IV., V., VI., and VII., are abnormal. As examples, the elements thallium, lead, and bismuth, may be taken;

TABLE XXV.—STRUCTURES OF Hg, Tl, Pb, Bi

Orbits.	1-5.	6s	6p
80 Mercury .	60, 18,	2	
81 Thallium .	60, 18,	2	1
82 Lead .	60, 18,	2	2
83 Bismuth .	60, 18,	2	3

whilst mercury, although not falling in the above groups, may be added, since it shows similar abnormalities. If the electronic structures of these elements are written down (Table XXV), it is seen that the valency of mercury should be two; of thallium, three; of lead, four; and of bismuth, five, or three. The valencies actually exerted are: mercury, two; thallium, one and three; lead, two and four; bismuth, three, four and five and, possibly, two. Why is this?

It is now known that the first two electrons in any group, having the quantum numbers Ns , behave differently from the rest, as they correspond to the $1s$ electrons in helium. They form a subsidiary stable arrangement, and may be difficult to ionise, or even to share. They are called an "inert pair".

In the instance of mercury, the mercurous ion has been shown by Ogg, and others, to be $[Hg_2]^{++}$ and not $[Hg]^+$. In the mercury atom, the structure ends with two $6s$ electrons, and if the theory of the "inert pair" is correct, mercury should be a comparatively inert element. The structure of the mercurous ion is evidence for this. In this, there are two mercury atoms sharing two electrons, thus giving the "ion" two positive charges. Since the $6s$ electrons can link together the two mercury atoms, they form covalent rather than electrovalent linkages. This is shown again in the unusual fact that mercuric salts are, on the whole, little ionised. They are predominantly covalent compounds. The conductivity of a solution of mercuric chloride is much smaller than that of an equivalent solution of, say, cadmium chloride.

With thallium, the two $6s$ electrons and the one $6p$ electron can be used for covalencies, but only the $6p$ electron can be used for electrovalencies. Thus, the thallic salts are ionised, but the thallic salts are all covalent, and do not ionise. With lead, the bivalent compounds, such as lead nitrate, $Pb(NO_3)_2$, are electrovalent and ionised in solution, whilst the quadrivalent compounds, such as lead tetrachloride, $PbCl_4$, are definitely covalent.

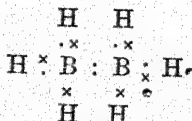
In bismuth the two 6s electrons are similarly inert as regards valency, for bismuth never forms electrovalent compounds with a valency greater than three. Tin shows similar behaviour to lead. Its structure is 2, 8, 18, 18, 2, 2; the two 5s electrons are an inert pair. The quadrivalent salts of tin, such as stannic chloride, are covalent, whilst the bivalent salts, such as stannous chloride, are electrovalent.

78. Distinction between Electrovalent and Covalent Compounds.—

In an electrovalent compound there will be no definite structural bond, but a strong electrostatic field, and so the work done in separating molecules will be greater than the work required to separate molecules in covalent compounds. This means that the boiling point of an ionised compound will be much higher than that of a covalent compound, and this is found to be so in the vast majority of cases. Thus carbon tetrachloride may be compared with common salt. The boiling point of the former is 78° C., whilst that of the latter is over 1,000° C. Or, compare stannic chloride, which is a liquid, and potassium chloride. The first is a typically covalent compound, the latter a typically electrovalent compound.

It is found, too, that covalent compounds are soluble in normal solvents, such as benzene and ether, whereas electrovalent compounds are soluble in abnormal liquids like water, which cause ionisation.

Lewis pointed out that linkages always appeared to involve two electrons—electron pairs, he called them. It is possible, however, that single electron linkages can exist. One instance where the existence of singlet linkages has been postulated is in the hydrides of boron. A series of these has been investigated by Stock, and the hydrides are found to have the formulæ corresponding to the hydrocarbons. The most common boron hydride has the formula B_2H_6 , which, by analogy with ethane, would be expected to be derived from a tetravalent atom. Boron, however, is trivalent. One way of explaining the existence of these compounds is to assume that some of the hydrogen atoms are linked to the boron by singlet linkages, as the following formula shows:—



The structure of the boron hydrides is still, however, an open question.

79. Fajans' Rule.—Fajans' rule¹ concerns the occurrence of electro- and co-valencies, and its connection with the position of the element in the Table. It states that the formation of electrovalent linkages is promoted by a high atomic volume (atomic weight divided by specific gravity) for the cation as compared with the anion, and by small ionic charges. There is considerable theoretical basis for this. It is clear that

¹ See also § 140.

the larger a metallic atom the less will be the attractive force for the outer electrons. They will not be held so strongly by the nuclear charge. The formation of a cation is thus helped by a large atomic volume, and of an anion by small atomic volume. The formation of multivalent anions (with the exception of complex ions, such as $[\text{Fe}(\text{CN})_6]^{4-}$) is an extremely difficult matter, since every addition of electrons makes the nuclear attraction smaller. A simple analogy is that of a magnet picking up nails successively. As each one is added the attraction for more gets less. It is for this reason that the maximum valency for a simple anion is two, whilst the valency of a cation can go up to four. Summing up, the conditions tending to produce electrovalent and covalent compounds are as follows:—

Electrovalent.	Covalent.
Low charge.	High charge.
Large positive ion.	Small positive "ion".
Small negative ion.	Large negative "ion".

It must be mentioned that whilst Fajans' rule is very helpful, it is not without exceptions.

The alkali metals (lithium, sodium, potassium, rubidium, and caesium) form good examples of the application of Fajans' rule. The atomic volumes of these elements are shown in the Table.

TABLE XXVI.—ATOMIC VOLUMES OF THE ALKALI METALS

Metal	Li	Na	K	Rb	Cs
Atomic Volume	11.8	23.7	45.3	56.0	70.7

The atomic volumes of the last three elements are very large. This means that the valency electrons have large orbits, and will be comparatively easily detached. The charge, of only one unit, on the ion, also adds to the ease of ionisation, according to Fajans' rule. Thus, except for lithium and sodium there is little tendency for these elements to form covalent bonds. Hydration of salts is an indication of formation of a co-ordinate link, as in solvation of ions (§ 75). Accordingly, it is found that the salts of lithium are nearly all hydrated, and so are many of those of sodium, thus showing the capacity of these elements to form covalent linkages (for a co-ordinate linkage is merely a form of covalent linkage). The salts of potassium, however, are seldom hydrated, whilst it is rare to find hydrated salts of rubidium or caesium.

Beryllium, in Group II., has an atomic volume of only 4.92, and a charge of 2 units. It is on the limit of ionisation, as would be expected from Fajans' rule. Magnesium has a high atomic volume (14.0), and though still capable of forming complexes, its compounds are predominantly electrovalent, and it resembles the alkaline earth metals much more than beryllium does.

In Group III., boron is unable to form a simple cation, owing to its small size (atomic volume, 4.11). Aluminium, having a larger atomic volume than beryllium (10.2), can form a trivalent cation, though the high charge (3) makes it form covalent compounds readily. Thus, aluminium chloride is a covalent compound in the solid state. It will readily dissolve in normal liquids, such as benzene.

An ion with a charge of 4 units could only exist if it were unusually large, and so none of the early elements in Group IV. are found to give electrovalent compounds. The first quadrivalent ion is found with tin (atomic volume 16.5).

It should be mentioned that there is some evidence for the existence in crystalline compounds of bonds intermediate in character between covalent and electrovalent bonds. For example, interatomic distances, determined by X-ray diffraction, or by electron diffraction, do not always correspond with those expected if the molecule were either covalent or electrovalent, but are intermediate in value. In many cases there seems to be resonance (§ 81 and 83) between electrovalent and covalent structures.

80. The Covalent Bond.—The wave-mechanical picture of the covalent bond visualises two electrons moving in an orbital common to the two atoms. This orbital, called a molecular orbital, is a region in space which embraces the two nuclei, and in which the electrons in the molecule are to be found most of the time. A molecular orbital arises from the overlap of two atomic orbitals, this overlap being the maximum possible. The two electrons in a covalent bond have opposite spins.

The simplest example of a covalent bond is found in the hydrogen molecule. Here the 1s-orbitals of the hydrogen atoms overlap to form a molecular orbital of the type known as a σ -orbital. This is sausage-shaped (Fig. 43).

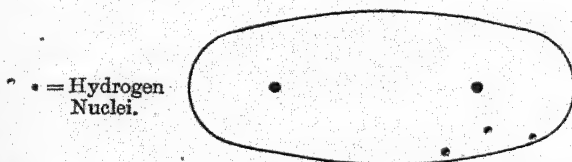


FIG. 43.— σ -Type Orbital.

The stability of the covalent bond is due mainly to a phenomenon known as exchange. In a covalent bond each electron is no longer confined to a single nucleus, as it would be in an isolated atom. Both electrons are free to move in the fields of the two nuclei of the atoms linked by the bond. A particular electron is no longer identified with a particular nucleus, but the electrons continually exchange between the fields of the nuclei. The result of this exchange is a lowering of the

energy of the system and hence an increase in stability. In other words, the exchange gives rise to a force of attraction between the nuclei leading to the formation of a covalent bond. The force resulting from the exchange arises in the wave-mechanical treatment of the covalent bond; such forces do not occur in the classical theory. The energy gained in the exchange is known as the exchange energy.

The wave-mechanical picture serves as a guide to the shape of the molecule. Consider the water molecule as an example. The electronic configuration of oxygen is $1s^2 2s^2 2p^4$. The electrons which go to form a covalent bond are the unpaired electrons. In the $2p$ shell of oxygen there are two unpaired electrons; let us assume that one is in the p_x and one in the p_y orbital. These unpaired electrons form covalent bonds with the two $1s$ electrons of the hydrogen atoms; two bonds are formed, one between the p_x electron and the electron of one of the hydrogen atoms, the other between the p_y electron and the electron of the second hydrogen atom. The bonds are formed where there is maximum overlap of the p and s orbitals. The p_x and p_y orbitals of oxygen are at right angles to one another, and so in their overlap with the s orbitals the resultant structure consists of two σ -orbitals at right angles to one another. Each orbital links the oxygen atom to one of the hydrogen atoms. The angle HOH evaluated experimentally is a little greater than 90° . This difference is due in part to the electrostatic repulsion of the hydrogen nuclei.

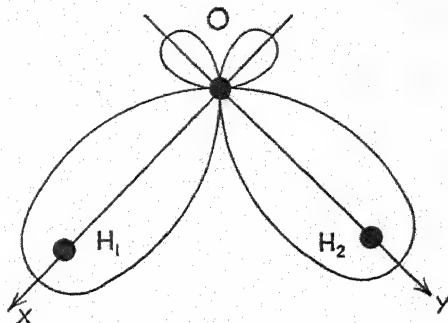


FIG. 44.—Water Molecule.

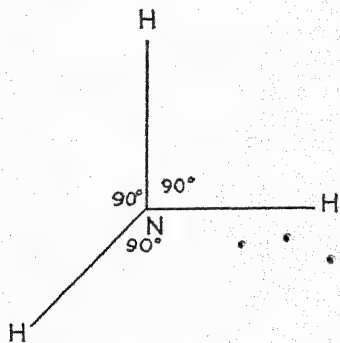


FIG. 45.—Ammonia Molecule.

$$\angle \text{HNH} = 90^\circ$$

forms a bond with an electron from one of the hydrogen atoms. This leads to an arrangement of bonds in the ammonia molecule, in which each nitrogen hydrogen bond is at right angles to the two other N - H bonds (Fig. 45). The lines in Fig. 45 represent the axes of the three orbitals.

The valency of carbon presents an important problem. Here the external configuration of the atom is $1s^2 2s^2 2p^2$. There are only two unpaired electrons, which would seem to indicate that carbon is divalent. Carbon, however, is almost always quadrivalent. To account for four unpaired electrons a process known as promotion is supposed to take place. In this process the electrons in the $2s$ shell uncouple and one is promoted to the p level giving an sp^3 configuration. A difficulty still remains. If the four sp^3 electrons formed bonds there would be three bonds at right angles to each other and a fourth bond with no directional properties. It has been known, however, for a long time that the valencies of the carbon atom point to the corners of a tetrahedron, of which the carbon nucleus is the centre. It is believed, therefore, that the process of promotion is followed by another process known as hybridization. In the latter the three p -orbitals and the s -orbital combine together to give four hybrid orbitals which are equivalent to each other and are arranged in tetrahedral fashion. It can be shown that this tetrahedral arrangement is the most stable one resulting from the combination of the s - and the three p -orbitals. This sp^3 hybridization of carbon takes place in most cases in which carbon is linked to four other atoms, as, for example, in the paraffins.

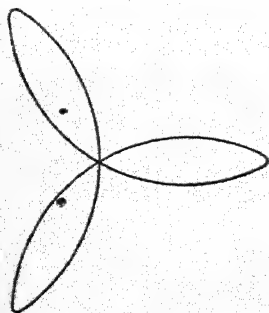


Fig. 46.— sp^2 -Hybridization in the Carbon Atom.

Where carbon is linked to three other atoms the four orbitals do not hybridize. Only the s - and two of the p -orbitals hybridize in this case; the other p -orbital remains unaffected. The result of this sp^2 hybridization is three orbitals the axes of which are coplanar at angles of 120° with each other (Fig. 46).

The ethylene molecule may be considered as an example of this type. The two carbon atoms undergo sp^2 hybridization. In each carbon atom two of the hybrid orbitals go to form covalent bonds with two hydrogen atoms and the third orbital forms the covalent link with the other carbon. The resulting structure is shown in Fig. 47. The six nuclei forming the molecule are coplanar. The p -orbitals unaffected by hybridization still remain to be considered. These two orbitals, one from each carbon atom, have a tendency to overlap; this tendency leads to the formation of a molecular orbital (Fig. 48). The molecular orbital formed from the p -orbitals not involved in the sp^2 hybridization has a different shape from a σ -orbital and is known as a π -orbital. It is in two sections, one above, the other below the plane of the nuclei. Thus the carbon atoms in ethylene are linked by two orbitals, one σ -type orbital and one π -type orbital. This constitutes a double bond.

Both the σ - and the π -orbitals contain two electrons.

It can be seen that an attempt to rotate one of the CH_2 groups in the ethylene molecule about the C-C axis of the molecule will result in a lessening of the overlap of the p -orbitals forming the π -orbital of the

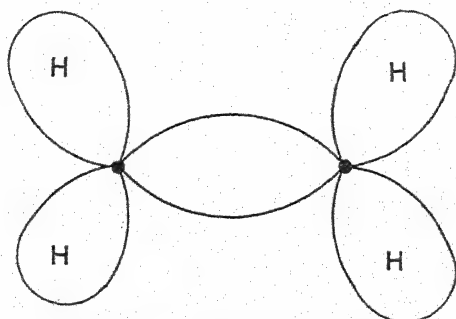


FIG 47.— σ -Orbitals of Ethylene.

double bond. This will decrease the stability of the bond. Hence there is no rotation of groups about a double bond; a double bond defines a plane. This explains the cis-trans isomerism of maleic and fumaric acids (Fig. 49, where the correct steric representations of the acids are given).

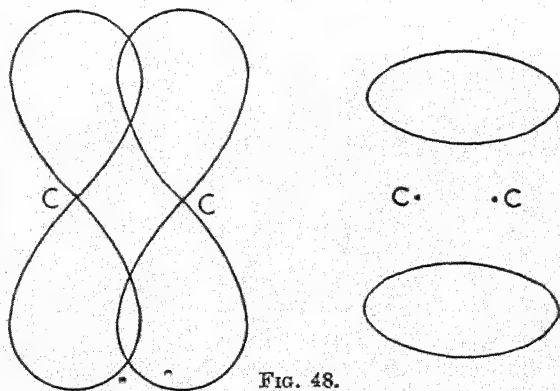


FIG. 48.

Electrons in a π -orbital are more accessible to attack from other molecules than are electrons in a σ -orbital. It is for this reason that a double bond is more reactive than a single bond.

81. Conjugated Systems of Double Bonds.—The idea of sp^2 hybridization helps in understanding the structure of the benzene molecule. Each carbon atom in a benzene ring is linked to three atoms; two of these are adjacent carbon atoms in the ring, and the third is a hydrogen atom. In order to give this structure, the electrons of each carbon atom undergo sp^2 hybridization. The three hybrid orbitals

form bonds with the atoms to which the carbon atom is attached. This results in the skeleton of the benzene molecule, which consists of a regular hexagon of six carbon atoms to each of which is linked a hydrogen atom. The twelve nuclei forming the molecule are coplanar. The skeleton is shown in Fig. 50.

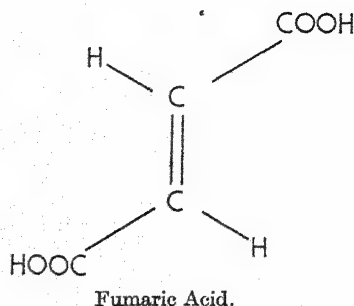
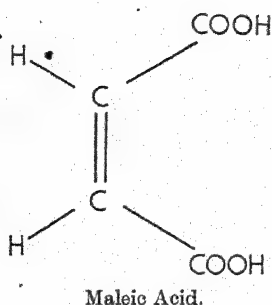


FIG. 49.

There is still one p electron on each carbon atom which has not taken part in hybridization. The orbitals of these electrons are shown in

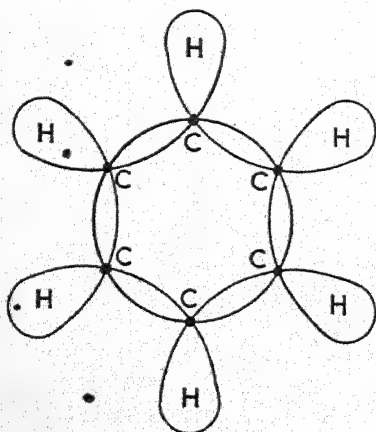
FIG. 50.— σ -Bond Skeleton of Benzene.

Fig. 51 (i). From the previous discussion on the double bond it may be expected that these p -orbitals will overlap with a neighbouring p -orbital to form a double bond. However, if any p -orbital in the ring is considered it can be seen that it has an equal tendency to overlap with each of its neighbouring p -orbitals. There is no more reason for the orbitals to overlap to link carbon atoms 1 to 2, 3 to 4, and 5 to 6 by π -orbitals than for them to overlap to result in π -orbitals between carbon atoms 2 and 3, 4 and 5, 6 and 1 (Fig. 51

ii, iii). Neither arrangement is more likely than the other. It is supposed, therefore, that these electrons are not confined to any particular portion of the molecule, but move in three delocalised orbitals. Each delocalised orbital embraces the six carbon nuclei. One such orbital is shown in Fig. 51. Two electrons of opposite spins occupy each orbital.

The behaviour of the delocalised electrons may be considered from another point of view. Neither Fig. 51 (ii) nor Fig. 51 (iii) gives an adequate representation of the benzene molecule. We suppose the

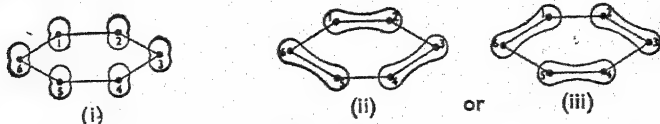
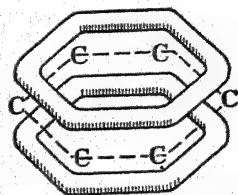


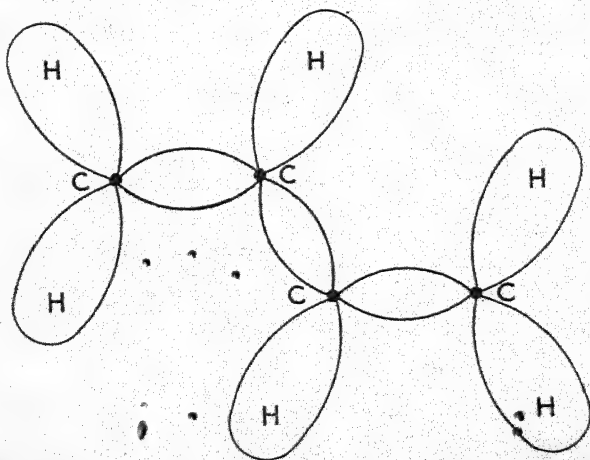
FIG. 51.

actual structure to be intermediate between the structures represented by Figs. 51 (ii) and 51 (iii). This intermediate structure is said to result from resonance of the extreme structures. These latter are called canonical forms, and the actual structure is called a resonance hybrid. The canonical forms contribute equally to the final structure. Resonance decreases the energy of the system and the decrease in energy is called resonance energy.

It can be seen that both conceptions of the π -electrons in benzene involve the idea that the electrons are no longer confined to a particular bond. Systems which involve delocalised electrons are called conjugated systems.

FIG. 52.—Delocalised π -Orbital of Benzene.

Butadiene is the simplest conjugated system. This is a hydrocarbon of molecular formula C_4H_6 , and we may consider its structure by a similar line of thought to that which we applied to the benzene structure.

FIG. 53.— σ -Orbitals of Butadiene.¹

¹ There is another form of butadiene which corresponds to the steric form shown in Fig. 53A but the form given in Fig. 53. is more stable at room temperature.

The sp^2 hybridization of the four carbon atoms leads to the skeleton of σ -bonds shown in Fig. 53. One p electron is left on each carbon atom. These p -orbitals overlap giving delocalised orbitals. The four electrons are re-accommodated in two delocalised orbitals, each orbital containing two electrons of opposite spin. One such orbital is shown in Fig. 54.

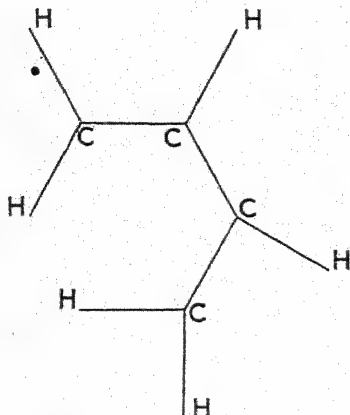
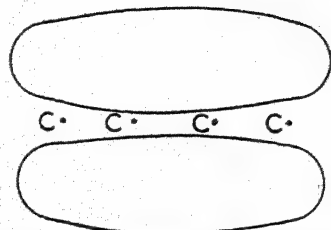
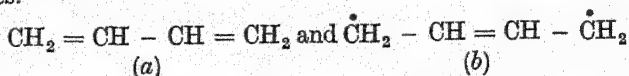


FIG. 53A.

FIG. 54.—Delocalised π -Orbital of Butadiene.

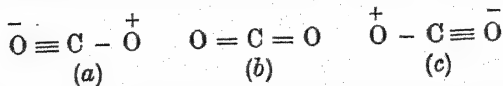
The butadiene molecule involves the resonance of two canonical structures:



Structure (a) is thought to contribute more to the final structure than does structure (b), which involves lone electrons on the terminal carbon atoms.

82. sp -Hybridization.—When a carbon atom is linked to only two other atoms sp -hybridization takes place. In this type of hybridization two of the p -orbitals of the carbon atom are unaffected. The sp -hybrid bonds are colinear. The two carbon atoms in acetylene molecule undergo sp -hybridization. This leads to the formation of a σ -bond between the carbon atoms and between each carbon atom and a hydrogen atom. The four nuclei of the molecule are colinear. If the p_z orbitals of the carbon atoms are involved in the sp -hybridization, then the p_x orbital of one carbon atom will overlap with the p_x orbital of the other carbon atom to give one π -orbital. This will be above and below the yz plane. Similarly the p_y orbitals of the two carbon atoms will overlap to give a second π -orbital that will be above and below the xz plane. This means that the triple bond will consist of one σ - and two π -orbitals.

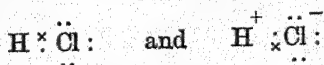
83. **Resonance.**—Resonance, which has already been discussed in connection with the structure of benzene (§ 81), occurs when the electronic structure of a molecule can be written in two ways of approximately equal energy and in which the positions of the atoms remain unchanged. The actual electronic structure is to be regarded as a combination of the various possible structures. For example, three electronic structures can be written for the carbon dioxide molecule:



There is resonance between the three structures, or canonical forms. The contributions of the ionic type structures (a) and (c) introduce a certain amount of triple bond character to the carbon-oxygen bonds, with the result that the carbon to oxygen bond-lengths in carbon dioxide are slightly smaller than the normal carbon-double bond-oxygen distances.

The effect of resonance on bond-length is also observed in the benzene molecule. The carbon to carbon single bond length is 1.54 Å; the carbon to carbon double-bond length is 1.33 Å. In benzene the carbon to carbon distance is 1.39 Å. This length is intermediate between that of single and double bonds and shows that the actual bonds in benzene are neither single nor double, but intermediate in character, the effect being due to resonance.

The bonds of a canonical form in a resonating system need not be covalent; electrovalent bonds can also be involved. Thus, hydrogen chloride can be represented both as a covalent and an electrovalent compound:



It is supposed that there is resonance between the two structures, so that the molecule is neither completely covalent nor completely ionic.

As a further example we may take the nitrous oxide molecule. Experiment shows that this molecule is linear, with the oxygen atom at the end of the line. There are two likely structures which fulfil this

condition, $\bar{\text{N}} = \overset{+}{\text{N}} = \bar{\text{O}}$ and $\text{N} \equiv \bar{\text{N}} - \overset{+}{\text{O}}$, the + and - signs indicating the polarity of the atoms in the molecule. These two structures can be shown to differ only a little in energy, and have the necessary conditions for resonance. It is believed then that nitrous oxide is not actually represented by either structure. That this is true is clear from experiment, which indicates that the molecule does not possess a large dipole moment, as it would have if it were markedly polar as required by either of the above structures.

It should be emphasised that nitrous oxide is not a tautomeric

mixture of molecules with these two structures. Statistically, the real structure is something intermediate between the two, which cannot, in fact, be represented by the conventional diagrams. The stability of nitrous oxide is to be ascribed to the fact that the energy of the resonating system is less than that of either structure separately.

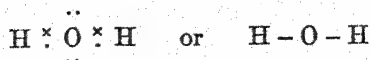
84. Complex Compounds.—The idea of hybridization can be applied to the clarification of the structure of complex compounds.

Consider the ferricyanide ion $[\text{Fe}(\text{CN})_6]^{--}$. The iron atom has the outer electronic configuration $3d^5 4s^2$. This means that the electronic shells up to and including $3p$ are fully occupied; the $3d$ level contains six electrons, while the $4s$ shell contains two electrons. The iron atom loses three electrons to give the ferric ion, which has the configuration $3d^5$. The ferric ion, with three positive charges, co-ordinates with six negatively charged CN ions to give a complex ion carrying three negative charges. The iron atom in the complex is linked covalently to each of the cyanide ions. The pair of electrons comprising each Fe-CN bond is supplied by the cyanide ion. Six unoccupied orbitals in the ferric ion are used in the formation of the bonds. The orbitals are the $4s$, the three $4p$, and two of the $3d$ orbitals. Before taking part in the bond formation the six orbitals hybridize. This hybridization is called a d^2sp^3 -hybridization. It results in the formation of six hybrid bonds which point along three axes at right angles. Such bonds are directed from the centre to the corners of a regular octahedron. This octahedral arrangement of the CN groups about a central iron atom is confirmed by experiment.

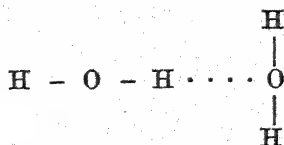
Hybridization involving d -orbitals can occur in other ways; thus dsp^2 -hybridization, which gives rise to a planar system of hybrid bonds, takes place in the $[\text{Ni}(\text{CN})_4]$ complexes.

85. The Hydrogen Bond.—Hydrogen behaves in a peculiar way in a number of compounds, and was at one time thought to be capable of forming a stable ring of four electrons. This is now known to be impossible, but of the existence of some sort of interaction between a hydrogen atom and other atoms there is no doubt. The effect is most pronounced when the hydrogen is linked to oxygen or nitrogen (*i.e.*, in the groupings O - H and N - H) and the atom with which interaction takes place is F, Cl, N, or O. The term "hydrogen bond" was proposed by Latimer and Rodebush for this interaction, although, as no definite "bond" is involved, it is perhaps better to use the name "hydrogen bridge" suggested by Huggins, and used commonly in the American literature, or, since it is not the hydrogen atom itself that is involved, but the free proton, a "proton bond", as suggested by Palmer.

Experiment shows that water is associated. At ordinary temperatures the molecule consists of aggregates of three simple H_2O molecules. This simple molecule is represented on the electronic theory as



The hydrogen can form a "hydrogen bond" with the oxygen-atom of another H_2O molecule, thus



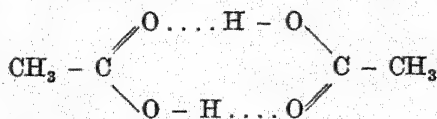
This may go on with the "addition" of another molecule of H_2O .

As far as theory is concerned, it is evident that this adding of H_2O molecules could go on indefinitely. It comes to a stop, however, when the thermal vibrations of the molecule become large enough to prevent it. At ordinary temperatures, then, the aggregate contains, as a rule, three simple molecules, and as the temperature is raised the proportion of dimeric molecules increases, and that of trimeric molecules decreases. The degree of association of water at different temperatures is given in the table in § 191.

Hydrogen fluoride is also associated for a similar reason.



Almost all organic hydroxy-compounds, such as alcohols, phenols, etc., are associated in the same way, and can be accounted for by hydrogen bonding. Hydrogen bonding occurs in the carboxylic acids,



leading to the formation of dimers.

It was proposed by Sidgwick that the hydrogen bond could be explained as a case of resonance, the proton forming the bridge being first nearer the one atom and then the other between which the bridge exists:



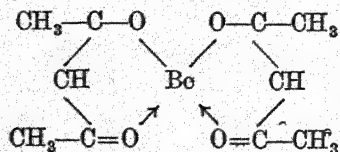
This view, however, is not now regarded as correct. It is more likely that the effect is electrostatic. The hydrogen ion is a bare proton with no electrons surrounding it, and would therefore be likely to attract other atoms, particularly electronegative ones. If this view is correct, the strongly electronegative elements, fluorine, oxygen, nitrogen, and chlorine would be expected to interact with hydrogen to form the

hydrogen bond, and these are, in fact, the very atoms which do. Fluorine, the most electronegative of these elements forms the strongest hydrogen bonds, oxygen weaker ones, and nitrogen weaker still. Chlorine, although as strongly electronegative as nitrogen does not form such powerful hydrogen bonds; Pauling regards this as due to the larger size of the chlorine atom, which causes its electrostatic attraction to be smaller.

Hydrogen bonds between carbon and oxygen or nitrogen are also known, but they are very weak.

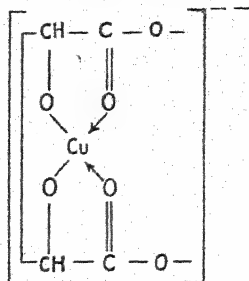
In addition to explaining the association of hydroxy-compounds, the hydrogen bond explains the structure of many hydrated salts, and of metallic hydroxides. It also has a very marked effect on the crystal structure and properties of many substances containing the OH group. The existence of $O - H \cdots O$ bonds explains the open type of lattice of a number of solid acids, *e.g.*, boric acid, where the molecules are linked in layers by hydrogen bonds, adjacent layers being held together only by weak forces (so-called van der Waals forces, § 87). This accounts for the softness of the crystals of this acid and their ready cleavage into thin layers. Bernal and Fowler have shown how the open structure of ice crystals is due to the same cause. This has many effects in nature, such as the expansion of water on solidification and the high latent heat of fusion of ice, facts of the greatest biological importance.

86. Chelate Compounds.—There are some peculiar metallo-organic compounds, in which there is internal co-ordination, which receive satisfactory explanation in terms of the electronic theory of valency. These compounds are called chelate compounds. In them a metal atom which might be expected to form an ion does not do so, but co-ordinates with another atom, usually oxygen. The metallic derivatives of the diketones fall into this class. The beryllium compound of acetylacetone $CH_3 \cdot C(OH) : CH \cdot CO \cdot CH_3$, may be represented as follows:—



The beryllium has its octet satisfied, and the compound is covalent.

A similar chelate group is probably present in Fehling's solution. This solution is prepared by adding a solution containing sodium hydroxide and sodium potassium tartrate to one of copper sulphate. In the absence of the tartrate the addition of the sodium hydroxide would precipitate copper hydroxide. With the tartrate, however, a deep blue solution is obtained, containing a complex copper ion which probably has the structure



87. Other Types of Bond.—For the sake of completeness it should be mentioned that two other types of bond are recognised—the van der Waals bond, and the metallic bond. The former is the weak force which exists between atoms and molecules with stable configurations and which holds such units together in the crystal lattice. The force is also operative, though to a smaller degree, in liquids and gases.

The bond holding metal atoms together is regarded as being different from the others studied because a flow of electrons is possible through the lattice, giving rise to electrical conductivity without the decomposition which accompanies electrolysis (see § 315).

Since the van der Waals and metallic bonds are not of great importance in chemistry they will not be considered in detail.

SUGGESTIONS FOR FURTHER READING

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CHAPTER V

THERMODYNAMICS—I

88. **Thermodynamics.**—Thermodynamics is the science that treats of energy changes. The name thermodynamics is a misnomer, and Guggenheim has suggested that the name thermophysics would be more correct for this branch of science. Many treatments of this subject are concerned with various types of heat engines, which are devices for converting heat into work; this is because the original and fundamental work was carried out by engineers. Actually the conclusions of thermodynamics are quite general since they apply to ideal systems. Thermodynamic reasoning is independent of the nature of the system and applies equally to the boiler of a steam engine and to the dissolution of the electrode in a galvanic cell. The methods of thermodynamics are those of an exact mathematical science. Since physical chemistry has a great deal to do with the energy changes in chemical reactions it is not surprising that a knowledge of at least the fundamentals of thermodynamics is an essential for the physical chemist.

There are three laws, or postulates, based on experience, which may be regarded as the starting points of thermodynamics, and the science is built up from these by purely logical reasoning.

89. **The First Law of Thermodynamics.**—The first law of thermodynamics is simply a statement of the principle of conservation of energy. This states that *although energy may be converted from one form to another it can neither be created nor destroyed.*

The exact equivalence of heat and mechanical energy is a corollary of the first law. When heat is added to a system the internal energy of the system increases; if the system does work it does it at the expense of the internal energy. The conversion of work into heat was first studied by Joule. He measured the amount of heat produced in a large number of different mechanical processes, and showed that its relationship to the energy expended is given by

$$E = JQ$$

where E is the work done, Q is the heat developed, and J is a constant known as the mechanical equivalent of heat, or Joule's equivalent. If E is measured in ergs and Q in calories, the value of J is approximately 4.2×10^7 ergs per calorie (or 4.2 joules per calorie).

The internal energy of a system is a function of the state of the system only. It does not depend on the way in which the system has

reached that particular state. For example, consider a system defined by the particular pressure, volume, and temperature at the point A (Fig. 55). The pressure, volume, and temperature are changed in such a way as to bring the system to a point B by path I and back to A by path II. The energy change involved in bringing the system to B by path I must be exactly the same as that involved in bringing the system back to A by path II. If the energy changes are not the same, then the system back in its first state will be associated with more or less internal energy than it had originally, and energy will have been created or destroyed. This is contrary to the first law of thermodynamics.

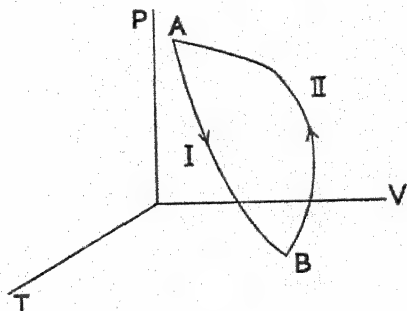


FIG. 55.

Heat absorbed by a system is given a positive sign, and that given out by a system a negative sign. Work done by a system is positive, and work done on a system is negative. It follows that if U is the internal energy, then

$$\Delta U = Q - W$$

that is, the increase in internal energy of the system (ΔU) is equal to the heat absorbed (Q) minus the work done by the system (W). In using such an expression (or indeed any mathematical formula applied to a scientific problem) it is necessary to express all terms in the same units, but this is generally understood when a formula such as the above is quoted. Thus, if a system absorbs 100 calories of heat, and does 5 joules of work, the increase in the internal energy will be $(100 \times 4.2) - (+5) = 415$ joules.

If it is assumed that heat is taken into a system at constant pressure P , the process will usually be accompanied by a volume change ΔV , and the mechanical work done by the system will be $P \Delta V$. If the absorption of heat Q_p at constant pressure changes the internal energy

of the system from U_a to U_b and the volume changes from V_a to V_b , then applying the equation

$$\Delta U = Q - W$$

we have

$$U_b - U_a = Q_p - P(V_b - V_a).$$

That is

$$\begin{aligned} Q_p &= U_b - U_a + P(V_b - V_a) \\ &= (U_b + PV_b) - (U_a + PV_a) \end{aligned} \quad (1)$$

P , and V , like U , depend on the state of the system, so a function H can be defined as follows:

$$H = U + PV.$$

H is called the heat content of the system. It depends only on the state of the system. It can be seen from equation (1) above that the heat absorbed in a process carried out at constant pressure is equal to the change in the heat content of the system, *i.e.*,

$$\Delta H = \Delta U + P\Delta V = Q_p.$$

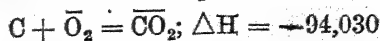
90. Thermochemistry.—Whenever any chemical reaction takes place, heat is either absorbed or evolved. This is due to the fact that chemical compounds have various amounts of energy associated with them, and as the energy of the products of a reaction is never equal to that of the reactants, heat is evolved or absorbed when the reaction takes place.

Heat is measured in calories. It is a common error to confuse temperature with heat, but temperature is merely the level of heat, determining whether heat will flow from one body to another placed in thermal contact with it. The gram-calorie is the amount of heat required to raise the temperature of 1 gm. of water through 1° C. As this value varies slightly with temperature, it is customary, for accurate work, to specify the temperature over which the gram-calorie is to be measured. As a rule, the degree specified is 14°–15° C., though other figures have been proposed.

Since the amount of heat evolved and absorbed in any chemical reaction taking place between the weights of substances represented by the formulæ in the equation is usually fairly large, and runs into thousands of gram-calories, it is sometimes convenient to use the kilogram-calorie, *i.e.*, the amount of heat required to raise the temperature of 1 kilogram of water through 1° C. It is one thousand times as large as the ordinary gram-calorie. The ordinary gram-calorie is written with a small "c" and the kilogram-calorie with a capital "C". The term "*heat tonality*" is sometimes used to denote the amount of heat associated with a chemical reaction.

91. Heat of Reaction.—The heat of reaction is defined as the number of gram-calories of heat *absorbed* when the reaction takes place

at constant pressure, in the direction indicated by, and between the amounts of substances shown in the equation. Thus, the equation



means that when 12 gms. of solid carbon combine with 32 gms. of gaseous oxygen to form 44 gms. of gaseous carbon dioxide, 94,030 gm.-calories are evolved. The heat of reaction is simply the change in heat

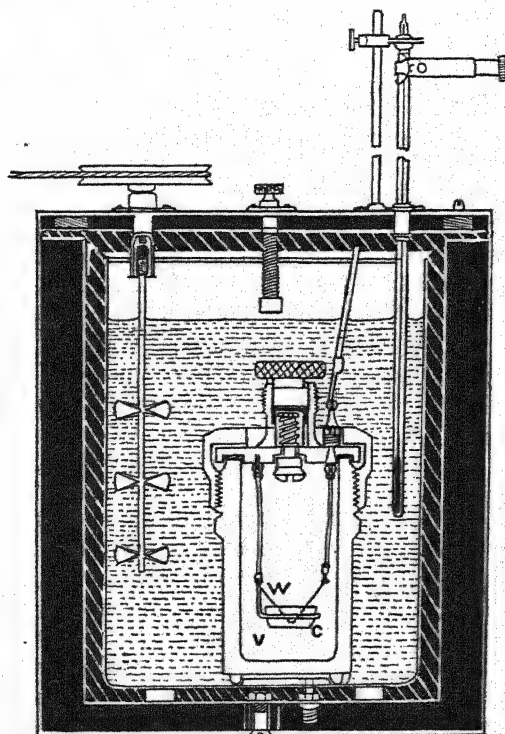


FIG. 56.—Berthelot's Bomb Calorimeter.

content that accompanies the reaction. It is necessary to specify the state in which the reactants or products are employed, or obtained, since heat will be absorbed or liberated in changes of state (*e.g.* from solid to liquid, or liquid to gas, or *vice versa*). This is indicated in the equation by putting a bar over the substance if it is a gas and a bar under it if it is a solid, and nothing at all if it is a liquid. Heat absorbed is given a positive sign, heat evolved a negative sign¹. This convention of sign is the one used throughout thermodynamics. The heat evolved in a reaction is lost by the system and so is given a negative sign.

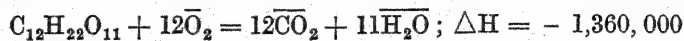
The symbol *aq* in a thermochemical equation signifies that the

¹ In some treatments of thermochemistry an opposite convention of signs is used.

substance is present with plenty of water, sufficient in fact to make the addition of any further quantity of it have no effect on the heat evolved. In this condition its *heat of dilution* is negligibly small.

Reactions are frequently classified according to type for thermochemical purposes, and the heats of reaction are given different names according to the type to which they belong. Thus there are heats of combustion, heats of formation, heats of neutralisation, heats of dilution, heats of dissociation, heats of atomisation, heats of precipitation, etc. They are all, however (with the possible exception of heat of dilution) heats of reaction.

92. Heat of Combustion.—The heat of combustion of a compound or element is *the change of heat content when one gram-molecule is burned in oxygen at constant pressure*. Thus



This means that when one gram-molecule of cane-sugar is burnt in excess of oxygen, 1,360,000 gm.-calories of heat are given out.

The heat of combustion is determined experimentally by means of Berthelot's Bomb Calorimeter. The general form of this apparatus is shown in Fig. 56.

The apparatus consists of a very strong vessel (V) and cover, made of steel, nickelled on the outside, and coated on the inside with some non-oxidisable material, such as gold, platinum or enamel. The cover is fitted to the vessel by a piece of metal screwed to the body of the bomb. Through the centre of the cover is an inlet tube and valve, through which oxygen can be passed. There is a platinum wire W connected to a platinum cup C, and another platinum wire which passes through an insulating washer in the cover. The purpose of this is to allow an electric current to be passed to start the combustion.

If the substance to be burnt is a solid, it is compressed into a cylinder; if a liquid, it is placed in the platinum capsule (C). The material is placed on the platinum support, and above it the two platinum wires W are joined by a thin spiral of iron wire. The bomb is closed and oxygen introduced through the inlet tube until there is a pressure of about 25 atmospheres inside. The screw valve is then tightened, and the bomb is immersed in water placed in a calorimeter. The temperature of the water is taken, and then the combustion is started. The temperature is then read every minute, and the results plotted. A

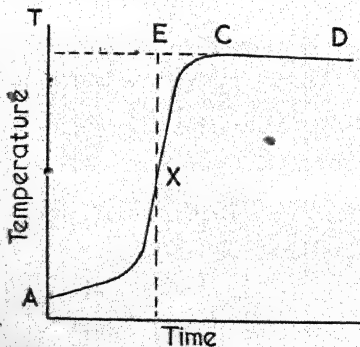


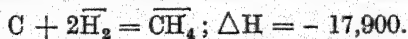
FIG. 57.

curve like that shown in Fig. 57 is obtained. By extrapolating, the maximum temperature attained during the combustion is obtained. The lower portion represents the variation of temperature of the calorimeter and contents with time before the reaction begins. When the reaction starts, the curve rises rapidly. CD represents the cooling with time. To obtain the maximum temperature actually reached during the reaction, draw a perpendicular through X, the mid-point of the rising portion, and produce CD backwards to cut it at E. The temperature T corresponding to this point E is the temperature required. For the calculation it is necessary to know the water equivalents of all the instruments used.¹ These have to be determined previously by immersing the instrument in water at a known temperature, and noting the decrease in temperature. The heat due to the combustion of the iron wire must be subtracted from the final result.

93. Heat of Formation. Intrinsic Energies.—The heat of formation is defined as *the change in heat content when one gram-molecule of a substance is formed from its elements at constant pressure.*

It is usually difficult to obtain the heat of formation of a compound directly, except where it is an oxide, and then the heat of formation coincides with the heat of combustion. Thus, it is not possible to make sodium hydroxide directly from its elements. In cases of this kind it is necessary to derive the heat of formation from the heats of other reactions, making use of Hess's Law (§ 94).

The heat of formation of a compound is an important constant for that compound. As will be seen later, it decides the stability of the molecule. The heat of formation will also give us information as to the amount of energy contained in a molecule. Thus, the heat of formation of methane is about $-17,900$ gm.-cals. This means that



Since, by the law of conservation of energy, the energy liberated in the form of heat cannot have come from nowhere, the elements carbon and hydrogen, from which the methane was made, must have altogether $17,900$ gm.-cals. more energy than the methane molecule. The methane itself must have $17,900$ gm.-cals. less energy than the elements from which it was made. This amount of energy associated with a compound is called its relative *intrinsic energy*. It is equal to the heat of formation of the compound with its sign changed. Since we are not yet fully acquainted with the intrinsic energies of elements, they are all placed arbitrarily at zero. We know this cannot be correct; it is highly unlikely that the energy content of all atoms should be the same. But our knowledge of the value of this intrinsic energy is not certain, so at the moment it is necessary for us to base our practical definition on the

¹ The water equivalent is the mass of water which would require the same quantity of heat to raise its temperature through 1°C. as is required by the instruments (calorimeter, thermometer, etc.) for this purpose.

older view that all elements have the same intrinsic energy, and this is placed arbitrarily at zero. The subject will be further discussed later (§ 100).

This convention makes it very easy to calculate heats of formation, etc. Thus, we see that the intrinsic energy of a compound is its heat of formation with the sign reversed. The intrinsic energy of 1 gm.-molecule of methane is 17,900 gm.-cals. The point to remember is that the sum of the energies on both sides of a thermochemical equation must be the same, in order to satisfy the law of conservation of energy.

An example of the use of this conception in the calculation of heats of formation may be given. From the heats of formation of carbon dioxide from carbon and from carbon monoxide respectively it is required to calculate the heat of formation of carbon monoxide.



The equation for the heat of formation of CO is



where x is the heat of formation.

From equation (1) the intrinsic energy of carbon dioxide is 94,030 cals. From equation (3) that of CO is $-x$. Writing the values of the intrinsic energies in equation (2), we have

$$-x - 0 = -94,030 - 67,300.$$

Hence,

$$x = -26,730 \text{ cals.}$$

94. Hess's Law of Heat Summation.—*If a chemical change can be made to take place in two or more different ways, then the amount of heat absorbed or evolved in the total change is the same no matter by which method the change is carried out.* This Law, which is merely a consequence of the First Law of Thermodynamics (Law of Conservation of Energy), was first stated by Hess in 1840. If the law were not true it would be possible to obtain energy without a corresponding expenditure of work, for suppose that, by taking the path AcB from A to B , a certain amount

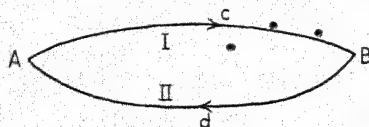


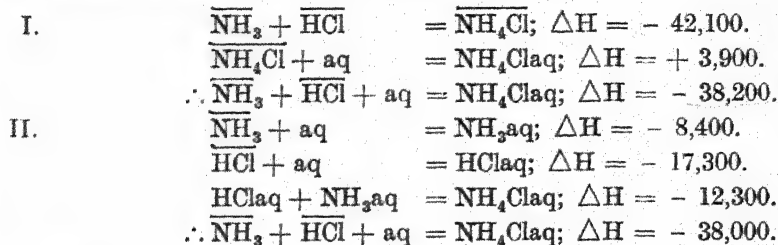
FIG. 58.

of heat is given out, whereas by going *via* AdB at the same temperature the amount of heat evolved is less than before. Then, by going *via* AcB , and returning *via* BdA , the amount of heat given out in the first minus that given out in the second would be available for external work.

The Law has been tested experimentally and found to be true. A good example is to calculate the heat of formation of a dilute solution of ammonium chloride from ammonia and hydrogen chloride. This can be done in two ways:—

(1) Prepare solid ammonium chloride from ammonia and hydrogen chloride. Then dissolve it in excess of water.

(2) Prepare a solution of ammonia and one of hydrogen chloride in equivalent amounts and mix the two. The amounts of heat evolved in these changes are given in the following equations:—



It is seen that the amount of heat evolved in the two methods is the same, within the limits of experimental error.

Hess's Law is of great practical importance, since it enables the heat of reaction to be calculated in cases where it cannot be measured directly. Thermochemical equations may be added or subtracted. Indeed, they may be regarded just as algebraical equations. In thermochemical calculations it is of the utmost importance to make certain of the sign of the heat (+ or -).

95. Exothermic and Endothermic Compounds.—Compounds which are formed with evolution of heat are called *exothermic compounds*. Those formed with absorption of heat are called *endothermic*. This fact about a compound is of very great importance, since it enables us to predict its stability. An endothermic compound will contain more energy than the substances from which it was made. If a compound is formed with absorption of heat, it follows from Le Chatelier's theorem (§ 149) that it will be stable at high temperatures. It will require high temperatures for its formation, since the absorption of heat tends to annul the constraint put on the system. Endothermic compounds are therefore not stable at low temperatures. They can be kept indefinitely at such temperatures by freezing the equilibrium (§ 198), but not otherwise.

Exothermic compounds will be stable at ordinary temperatures, but unstable at high temperatures, for a similar reason.

Among endothermic compounds are to be found the oxides of nitrogen, hydrogen iodide, ethylene, acetylene, ozone and hydrogen peroxide. These are all substances which are formed from their elements in appreciable quantities only at high temperatures.

96. Heat of Neutralisation.—The heat of neutralisation of an acid by a base is defined as *the amount of heat evolved when one gram-equivalent of the acid is neutralised by a base.*

For strong acids and bases the value obtained is constant, and equal to about 13,700 gm.-cals (see Table LXXXVI).

The reason for the constancy of the heat of neutralisation of a strong acid by a strong base is that the reaction is always merely the combination of hydrogen ions and hydroxyl ions to form undissociated water. Thus, when sodium hydroxide solution, of which the solute consists entirely of sodium ions and hydroxyl ions, is mixed with hydrochloric acid also consisting entirely of hydrogen ions and chloride ions and water, it forms sodium chloride, which can be regarded as completely ionised, and water. The reaction is therefore effectively the combination of hydrogen and hydroxyl ions.

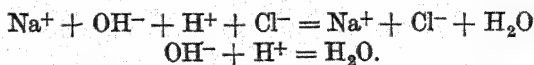


TABLE XXVII.—HEATS OF FORMATION

Substance.	Heat of Formation, gm.-cals.
Hydrogen chloride (gas)	– 22,000
Hydrogen bromide (gas)	– 8,440
Hydrogen iodide (gas)	6,400
Hydrogen fluoride (gas)	– 38,500
Carbon dioxide (gas)	– 94,030
Ammonia (gas)	– 11,000
Nitrous oxide (gas)	17,000
Nitric oxide (gas)	21,600
Nitrogen trioxide (gas)	22,200
Nitrogen dioxide (gas)	3,000
Nitrogen pentoxide (solid)	30,000
Hydrogen sulphide (gas)	– 5,200
Ozone (gas)	34,000
Hydrogen peroxide (liq.)	23,000
Water (liq.)	– 68,380

97. Determination of the Heat of Neutralisation.—The calorimeter used for this work must, of course, be made of glass. It may consist of two beakers separated from each other by cloth, or some other lagging material, or, better, it may be a vacuum flask. The latter makes a very efficient calorimeter.

In all calorimetric work it is necessary first of all to determine the water equivalent of the calorimeter and stirrer and thermometer. This is done by heating some water to the boiling point in a test-tube, taking its temperature, and then pouring it quickly into the calorimeter which has inside it the stirrer and thermometer to be used in the experiment. The temperature of the calorimeter may be taken as being the temperature of the room at the commencement of the determination. The temperature of the hot water in the calorimeter is taken every half minute, and the results plotted. A curve of the form shown in Fig. 57 will be obtained. If a vacuum flask is used the portion CD will be very nearly horizontal, and this may be taken as the temperature attained by the flask. Otherwise it will be necessary to extrapolate the portion CD back to the temperature axis. This point will be the temperature which the calorimeter would have reached had there been no loss of heat due to radiation and conduction.

The water equivalent of the calorimeter is its mass multiplied by its specific heat, and is represented by W . Then, if t_1 was the temperature of the calorimeter before the hot water was added, t_2 its temperature afterwards, t_3 the temperature of the boiling water, and m the mass of the hot water, then the heat given out by the boiling water is $m(t_3 - t_2)$ gm.-cals. That taken in by the calorimeter is $W(t_2 - t_1)$ gm.-cals. These two amounts of heat must be equal.

$$W(t_2 - t_1) = m(t_3 - t_2).$$

This equation gives W . To determine m , the water from the calorimeter is poured into a weighed flask and weighed.

Take 50 c.c. of normal sodium hydroxide and note its temperature (t_4), and 50 c.c. of normal hydrochloric acid, and note its temperature (t_5). The two temperatures will usually be the same, but they need not be. Pour the two solutions into the calorimeter, and take the temperature every half minute, the liquid being stirred all the time. Plot a cooling curve and extrapolate as before. If m_1 is the mass of the salt solution, and s its specific heat, and t_6 the final temperature, then the initial temperature of the liquid was $(t_4 + t_5)/2$, and the amount of heat given out must have been

$$m_1 s \left(t_6 - \frac{t_4 + t_5}{2} \right) + W(t_6 - t_1).$$

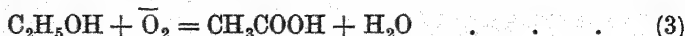
The value of $m_1 s$ may be taken as 100, since the mass will be a little over 100 gms., and the specific heat a little less than 1. The error in doing this will be less than 1 per cent. The value obtained must be multiplied by 20 to give the amount of heat evolved when 1 gm.-molecule of sodium hydroxide is neutralised by hydrochloric acid.

Similar apparatus and methods are employed for the determination of other heats of reaction.

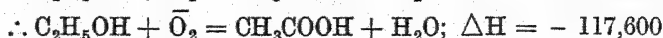
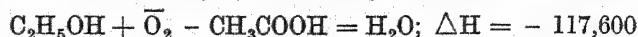
98. **Some Numerical Examples.**—(1) From the heat of combustion of ethyl alcohol and acetic acid respectively



calculate the heat of the reaction

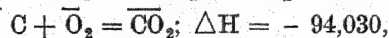
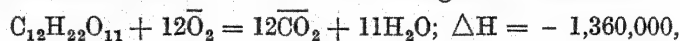


This can be obtained merely by subtracting (2) from (1). We have



The heat of the reaction is $-117,600$ gm.-cals.

(2) Calculate the heat of formation of cane sugar from the data

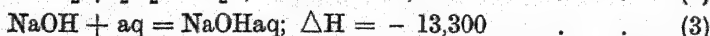
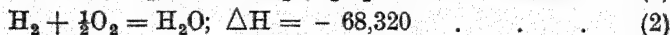
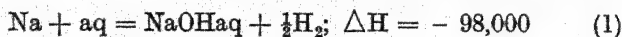


Let x be the heat of formation. Then $-x$ is the intrinsic energy. Substituting intrinsic energies in the first equation,

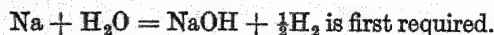
$$\begin{aligned} -x + 0 &= 12(94,030) + 11(68,320) - 1,360,000, \\ &= 1,128,360 + 751,520 - 1,360,000, \\ &= 519,880 \end{aligned}$$

\therefore The heat of formation is $-519,880$ gm.-cals.

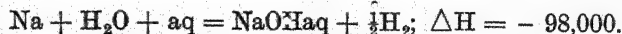
(3) Find the heat of formation of sodium hydroxide from the following data:—



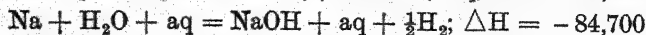
In equation (1) aq on the left-hand side includes the H_2O used up. The heat of the reaction



Rewriting (1),



Instead of NaOH_{aq} we may write from (3), $\text{NaOH} + \text{aq}$; $\Delta H = 13,300$



Let the heat of formation of NaOH be x . Its intrinsic energy = $-x$. Then substituting in (4)

$$0 + 68,320 = -x - 84,700.$$

$$\therefore x = -153,020 \text{ gm.-cals.}$$

The heat of formation is $-153,020$ gm.-cals.

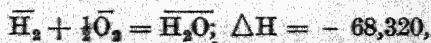
99. Correction of Thermochemical Data for Constant Pressure.—

All heats of formation and combustion are obtained for a system at constant volume. To find the heat evolved at constant pressure, a correction must be applied. At constant volume the reaction performs no external work. If, however, the reaction takes place at constant pressure, and this causes an increase in volume of v , then external work is done to the extent of pv . This amount must be added to the heat evolved at constant volume to obtain that at constant pressure. For liquids and solids the amount of the correction is small, since they undergo little expansion on heating under constant pressure; but for gases it may be considerable, and must be calculated for each individual case from the data given.

100. Heats of Atomisation.—Modern research in thermochemistry centres round the determination of the heat evolved in the rupture or formation of the various possible linkages, such as the covalent link (§ 74), and the semipolar double bond (§ 75). We have previously taken the intrinsic energies of the elements as zero. This assignment of zero energies is purely arbitrary, and is used because we are normally interested in the changes in energy that take place in a reaction. The energies of the elements do not change in the reaction, and hence they need not be taken into account. They are therefore placed arbitrarily at zero, though this is obviously not correct. Carbon in the form of diamond is a complicated structure of atoms joined together by certain bonds. When carbon dioxide is formed out of it, all these bonds have to be broken, and energy will be required for this. Similarly, the oxygen molecule has to be broken down to its atoms before it will combine with carbon to form carbon dioxide. Here again links have to be broken, and it is highly unlikely that the links between the oxygen atoms will have the same energy content as those between the carbon atoms in the diamond. Hence, it would be untrue to say that the intrinsic energies of these two elements are the same and can be placed arbitrarily at zero.

To discover the energy associated with the links which hold atoms together in molecules it is necessary to find the heat of atomisation, of the elements. Where the element is a diatomic one, all that has to be done is to determine its heat of dissociation into atoms. This heat can be determined in several ways; though most of them, and particularly those which are generally applicable, depend upon a study of spectra, the theory of which we cannot consider here. Suffice it to say that these values have been determined and are collected together in Table XXVIII.

101. Heats of Formation of Linkages.—Knowing the following heats of combustion



and one or two others, it is possible to calculate the heat of formation of many organic substances from their elements, since their heats of combustion are known. But this ordinary heat of formation from the elements, which we may call H_f , does not include the heat of atomisation of the elements. The heat of formation of the compound from its constituent atoms will therefore be given by H_f + the heats of atomisation of the elements.

TABLE XXVIII.—HEATS OF ATOMISATION OF ELEMENTS
(Figures are given in kg.-cals. per gm.-atom)

Element.	State.	Heat of Atomisation.
Hydrogen . . .	Gas	51.7
Oxygen . . .	Gas	59.1
Nitrogen . . .	Gas	85.1
Carbon . . .	Solid	124.3
Fluorine . . .	Gas	31.8
Chlorine . . .	Gas	28.9
Bromine . . .	{ Gas	26.9
	{ Liquid	28.7
Iodine . . .	{ Gas	18.0
	{ Solid	25.5
Sulphur . . .	{ S ₂ gas	52.0
	{ Rhombic	66.8

Thus, for methane, the heat of combustion is - 212.7 kg.-cals.
Hence, its heat of formation is

$$H_f = 212.7 - (94.03 \times 1) - (68.32 \times 2) \\ = - 17.9.$$

To obtain the atomic heat of formation, H_a , we must subtract the heats of atomisation of one C and four H = $124.3 + (4 \times 51.7) = 331.1$.
Hence, $H_a = - 349.0$ kg.-cals.

Now consider ethane, C_2H_6 . Its heat of combustion is - 368.3 kg.-cals. Hence,

$$H_f = 368.3 - (94.03 \times 2) - (68.32 \times 3) \\ = - 24.72$$

$$H_a = - 24.72 - (2 \times 124.3) - (6 \times 51.7) \\ = - 583.52 \text{ kg.-cals.}$$

From these two observations it is possible to calculate the heat of rupture of the C—H and the C—C links. We must assume that the heat of rupture is the same in both compounds.

Let x be the heat of rupture of the C—H link, and y that of the C—C link. Then, since methane contains four C—H linkages, presumably all the same, $4x = 349.0$ and $x = 87.2$ kg.-cals.

Now in ethane we have six C—H linkages, and one C—C linkage. Hence, $6x + y = 583.52$ and $y = 60.3$ kg.-cals.

TABLE XXIX.—HEATS OF FORMATION OF LINKS
(In kilogram-calories.)

Link.	Heat.	Substances.	Link.	Heat.	Substances.
H—H	103.4	H ₂ gas	C = S	130.9	Isothiocyanates
C—C	60.0	Diamond	C—Cl	66.5	Alkyl chlorides
¹ Cal—Cal	60.3	Paraffins	C—Br	54.0	Alkyl bromides
Cal—Car	79.40	Aromatic	C—I	45.5	Alkyl iodides
Car—Car	97.17	Aromatic	N≡N	208	N ₂ gas
C = C	123	Olefines	N—H	89.8	Ammonia
C≡C	161	Acetylenes	N—N	87.0	Alkylamines
Cal—H	87.4	Paraffins	O = O	118	O ₂ gas
Car—H	101.73	Aromatic	O—H	110	H ₂ O gas
C—N	48.6	Alkylamines	O—H	106	Alcohols
C = N	125.3	Iso cyanates	S = S	104	S ₂ gas
C≡N	183.0	Cyanogen	S—H	87.5	H ₂ S
C≡N	187.5	Acetonitrile	S—H	85	Mercaptans
C≡N	183	Iso cyanides	Se—H	73.0	H ₂ Se
C—O	76.5	Ethers	Te—H	ca 54	H ₂ Te
C—O	79.5	Acetals	F—F	63.5	F ₂
C = O	160	Aldehydes	Cl—Cl	57.8	Cl ₂
C = O	167	Ketones	Br—Br	46.1	Br ₂ gas
C = O	182	Esters	I—I	36.2	I ₂ gas
C = O	181.3	Carbon dioxide	F—H	147.5	HF
C≡O	235.5	Carbon monoxide	Cl—H	102.7	HCl
C—S	62	Alkyl sulphides	Br—H	87.3	HBr
C—S	54.5	Thiocyanates	I—H	71.4	HI
C = S	128.6	Carbon bisulphide	N—F	68.8	NF ₃
N—Cl	59	Cl—N = O	Cl—F	86.4	ClF
N—O	64.2	Methyl nitrite	Cl—Br	52.7	ClBr
Cl—O	49.3	Cl ₂ O	Cl—I	51.0	ICl
N = O	125	Nitrous oxide	Br—I	42.9	IBr

¹ Cal and Car stand for a carbon atom in an aliphatic and an aromatic compound respectively.


These values can be tested independently of a knowledge of heats of atomisation by considering the homologous paraffin series. If the energy associated with the linkages is the same in all the paraffins, then the heat of combustion, and the heat of formation from the elements H₂, and the heat of formation from the constituent atoms, will all differ by the same amount on passing from one member to the next. This is found to be the case.

The heat of rupture of these linkages can be determined by other methods, mainly spectroscopic, which give results in good agreement with those obtained from the thermochemical data.

When we treat other linkages in this way, and try to verify our conclusions by considering homologous series, the results are not so fortunate as with hydrocarbons. Thus, if we take the series of ketones, we find that the increase in the heat of formation for addition of CH_2 varies as the series is ascended. Hence, the value of the energy of the link must increase as the series is ascended. At present there is no satisfactory explanation of this, though several have been advanced. The heats of formation of various linkages are given in Table XXIX.

102. Application of Thermochemical Data to Structural Problems.—

The fact that the heats of formation of links depend upon the nature of the link (single, double, or triple bond, for instance) makes it possible to use thermochemical data for the elucidation of structure in some cases. For example, the structural formula of ozone in which the oxygen

atoms are linked with single bonds, , cannot be correct, since

the heat of formation calculated for this structure is -75.6 kg.-cal., whereas the observed value is -34.5 kg.-cal.

Heats of formation and combustion have also been useful in the study of the stability of organic compounds.

103. Kirchoff's Relationships.—These give the relation between the heat of a reaction and temperature. A process is carried out in which reactants in state A at temperature T_1 are converted into products in state B at temperature T_2 . It is assumed that all operations are carried out at constant pressure.

The reaction may be carried out in two ways. The reaction may be carried out at temperature T_1 and the products brought to temperature T_2 . Alternatively the reactants may be brought to temperature T_2 and the reaction carried out at this temperature. According to Hess's law the heat change should be the same whichever method is chosen.

If the reaction is carried out at temperature T_1 , the heat of reaction is the heat of reaction from A to B at T_1 , symbolised by ΔH_1 . The products must be heated from T_1 to T_2 and if the heat capacity of the system at constant pressure in the state B is C_p^B then the heat absorbed in going from A (T_1) to B (T_2) is

$$\Delta H_1 + C_p^B (\Delta T) \quad \dots \dots \dots (1)$$

where $\Delta T = T_2 - T_1$.

If the temperature were raised first to T_2 and the change from A to B carried out at this temperature, the heat absorbed is

$$C_p^A(\Delta T) + \Delta H_2 \quad (2)$$

where ΔH_2 is the heat of the reaction at temperature T_2 . By Hess's law (1) and (2) are equal, so

$$\Delta H_1 + C_p^B(\Delta T) = \Delta H_2 + C_p^A(\Delta T)$$

or

$$\frac{\Delta H_2 - \Delta H_1}{\Delta T} = C_p^B - C_p^A = \Delta C_p \quad (3)$$

where ΔC_p represents the change in heat capacity between the products and the reactants. If ΔT is small the equation may be written as a differential

$$\left(\frac{\delta(\Delta H)}{\delta T} \right)_p = \Delta C_p \quad (4)$$

If the process is carried out at constant volume, then the relationships

$$\frac{\Delta U_2 - \Delta U_1}{\Delta T} = \Delta C_v \quad (5)$$

and

$$\left(\frac{\delta(\Delta U)}{\delta T} \right)_v = \Delta C_v \quad (6)$$

can be obtained in a similar fashion.

The relationships (3), (4), (5), and (6) are called Kirchoff's relationships. It is important to note that in the derivation of the relationships (3) and (5) the heat capacities are assumed to be independent of temperature. This assumption does not apply to the derivation of (4) and (6) which, being in differential form, do not refer to a finite temperature range.

SUGGESTIONS FOR FURTHER READING

- SIDGWICK, N. V. "The Covalent Link in Chemistry," Chapter 4. (Cornell University Press, 1933.)
- PAULING, L. "The Nature of the Chemical Bond." (Cornell University Press, 1945.)
- GLASSTONE, S. "Thermodynamics for Chemists." (D. Van Nostrand Co., 1947.)

CHAPTER VI

THERMODYNAMICS—II

104. The Second Law of Thermodynamics.—It will be recalled that first law of thermodynamics states that in a particular process the energy difference between the final and the initial states is equal to the heat absorbed by the system less the work done by the system. It gives no information as to whether any particular change will take place spontaneously. The second law of thermodynamics can be used to predict the direction of a spontaneous chemical change under a given set of conditions. To facilitate discussion of this law various processes will first be considered.

Planck has divided all processes into three classes, natural, unnatural, and reversible.

Natural processes are all such as actually occur in nature. They always tend towards equilibrium. A system is in equilibrium when its properties do not change with time. Unnatural processes are those which move in a direction away from equilibrium, and they do not occur in nature. Reversible processes constitute a limiting case between natural and unnatural processes. Reversible processes, also, do not occur in nature. In a reversible process the system is always in equilibrium so that an infinitesimal increase in the tendency opposing the process will cause its reversal. Reversible processes must take place in infinitesimal steps. They can be defined generally as processes which can be performed in either of opposite directions, so that all changes occurring in any part of the direct process are exactly reversed in the corresponding portions of the reverse process. A reversible process is a continuous sequence of equilibrium states.

An example will make the idea clearer. Consider a system consisting of a liquid and its vapour at temperature T . Assume that the pressure in the system is P , and the vapour pressure of the liquid is p . Evaporation is taken as the process under investigation. If p is greater than P then the evaporation is a natural process and will take place. If p is less than P the process is unnatural and will not take place; the contrary process, condensation, is now the natural process. If p is equal to P then both condensation of the vapour and evaporation of the liquid are reversible processes. By an infinitesimal increase or decrease of P each process can be made to take place in turn.

Mathematically the situation can be summed up by saying that if

$P = p - \delta$ ($\delta > 0$) then evaporation is a natural process. In the limit $\delta \rightarrow 0$ the process becomes reversible.

Consideration must be given to the question of spontaneous change, that is, the type of change involved in natural processes. If a gas in a compartment is separated from a vacuum by a wall, and a valve between the two compartments is opened, the gas will expand through the valve into the vacuum and the process will continue until equilibrium is established, i.e., until the pressure throughout the system is uniform. Then again, if the two compartments contain different gases and the valve is opened, the different gases will diffuse until each is distributed uniformly throughout the other. Again, if one end of a bar is heated and the bar is then insulated, heat will be conducted to the unheated portion of the bar until it is all at the same temperature. All these processes are spontaneous. Further, they do not reverse themselves. Thus, the pressure distribution through a gas at equilibrium in a compartment remains uniform. Regions of differing pressure do not build themselves up. This may be generalised to the statement that spontaneous processes are irreversible, and this statement really constitutes the second law of thermodynamics. The second law has been stated in very many ways. We may state it here as follows: *It is impossible to construct a machine functioning in cycles which can convert heat completely into the equivalent amount of work without producing changes elsewhere.* This can be simplified to the statement that heat cannot be completely converted into work at one temperature. Another way of stating the second law is that *heat cannot of itself, without the intervention of an external agency, pass from a colder to a hotter body.*

105. Cyclic Processes.—A cycle is a process in which a system returns to its original state after a succession of changes. The change in internal energy brought about in a cycle is obviously zero. It follows that the heat supplied to the system less the heat given out during the process is equal to the work done in the cycle (all quantities being expressed, of course, in the same units). For a process in which heat is supplied and work is done the efficiency of the process may be

defined as $E = \frac{W}{Q}$ where W is the work done by the system and Q is

the heat supplied; the efficiency shows the fraction of the heat supplied that is utilised as work.

Two theorems can be proved from the second law of thermodynamics concerning a cyclical process functioning between two temperatures T_1 and T_2 .

The first of these states that the efficiency of a system working in a reversible cycle between the temperatures T_1 and T_2 depends only on these temperatures. The proof is as follows:

Assume that there are two processes α and β in which a system can

work in a reversible cycle between two temperatures T_1 and T_2 . Let β be the more efficient process. Then

$$\frac{W_\beta}{Q_\beta} > \frac{W_\alpha}{Q_\alpha}$$

At temperature T_1 in process β the system takes in heat Q_1 , does work, W_β , and cools to temperature T_2 , where it gives up heat $Q_{\beta 2}$. The cycle α is operated in an analogous manner, taking in heat Q_1 , doing work W_α , and giving up heat $Q_{\alpha 2}$. Assume the processes to be coupled so that β operates from T_1 to T_2 and α backwards from T_2 to T_1 . Then the coupled process involves the system in the following changes:

β : (1) takes up heat Q_1 at T_1 ; (2) does work W_β cooling to T_2 ; (3) gives up heat $Q_{\beta 2}$ at T_2 .

α : (1) takes up heat $Q_{\alpha 2}$ at T_2 ; (2) has work W_α done on it, heating the system to T_1 ; (3) gives up heat Q_1 at T_1 .

Applying the first law of thermodynamics,

$$Q_1 - Q_{\beta 2} = W_\beta$$

and
$$-Q_1 + Q_{\alpha 2} = -W_\alpha.$$

Hence
$$W_\beta + Q_{\beta 2} = W_\alpha + Q_{\alpha 2} \quad (1)$$

Because β was assumed to be more efficient than α

$$\frac{W_\beta}{Q_1} > \frac{W_\alpha}{Q_1}$$

Hence $W_\beta > W_\alpha$. It follows from equation (1) above that $Q_{\beta 2} < Q_{\alpha 2}$, i.e., $Q_{\alpha 2} - Q_{\beta 2} > 0$ so that at T_2 heat has been taken in by the system. Now the work done during the cycle is $W_\beta - W_\alpha > 0$; that is, the system has done work. At the higher temperature the system has taken in and given up the same amount of heat (Q_1). Hence, all the heat taken in at the lower temperature has been converted into work without other changes taking place. Thus, the process violates the second law and is therefore impossible. Now this process depended on the assumption that $E_\beta > E_\alpha$, so this must be untrue. It can be shown similarly that E_α cannot be greater than E_β . Hence $E_\alpha = E_\beta$.

The second theorem states that no cyclic process can be more efficient than a reversible one; it can be proved in a similar manner.

As shown above, the efficiency of systems working in reversible cycles depends only on the temperatures between which the cycle is working. Hence, to calculate the efficiency of *any* reversible cycle it is only necessary to consider one *particular* reversible cycle, and the one chosen for the purpose is that called the Carnot cycle.

106. Efficiency of a Reversible Cycle.—The Carnot cycle consists of four operations which are carried out on a system which is made up of one mole of an ideal gas. The gas is enclosed in a cylinder which is fitted with a weightless frictionless piston. All the operations in the

cycle are carried out reversibly. It is assumed that the system can be arranged so that some changes are carried out at constant temperature and these are known as isothermal changes. For other changes the system can be isolated in such a way that no heat can either enter or leave it, and these are known as adiabatic changes. Fig. 59 shows the pressure-volume changes during the cycle.

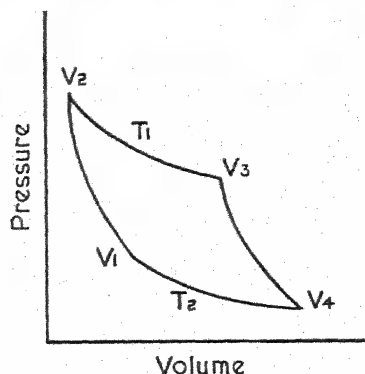


FIG. 59.—The Carnot Cycle.

Summary of the Cycle.

Volume change.	Operation.	Temperature.
(1) V_1 to V_2 .	Adiabatic Compression.	Rises from T_2 to T_1 .
(2) V_2 to V_3 .	Isothermal Expansion.	Steady at T_1 .
(3) V_3 to V_4 .	Adiabatic Expansion.	Falls from T_1 to T_2 .
(4) V_4 to V_1 .	Isothermal Compression.	Steady at T_2 .

The system is put through four reversible operations: It is compressed adiabatically from V_1 to V_2 and the temperature rises from T_2 to T_1 ; this is because work is being done on the system.

It is next expanded isothermally from V_2 to V_3 and then expanded adiabatically to V_4 during which the temperature drops to T_2 . Finally it is compressed isothermally to V_1 .

Consider first the two adiabatic changes. As no heat is supplied from the surroundings the work done causes an equivalent change in the internal energy of the system. In the first stage the temperature of the system rises from T_2 to T_1 . Hence the work done on the system is $C_v(T_2 - T_1)$, where C_v is the molal heat capacity of the gas at constant volume. The work done by the system in the other adiabatic stage is $C_v(T_1 - T_2)$. Thus, the work done by the gas in one adiabatic stage cancels out the work done on the gas in the other adiabatic stage.

Consider now the isothermal expansion and compression. If a gas expands by a volume dV against a pressure P the work done by the gas

is PdV . When the expansion is from V_2 to V_3 the work done is,

$\int_{V_2}^{V_3} PdV$. If the Carnot system contains one mole of an ideal gas

$PV = RT$, so $P = \frac{RT}{V}$. For an isothermal expansion at temperature

T_1 , the substitution of $\frac{RT_1}{V}$ for P in the integral gives the work done as

$$\int_{V_2}^{V_3} \frac{RT_1 dV}{V} = RT_1 \log_e \frac{V_3}{V_2}.$$

Corresponding to this work, heat Q_1 is taken in to keep the temperature constant. During the second isothermal stage the gas gives out heat

$-Q_2$ while work $RT_2 \log_e \frac{V_1}{V_4}$ is done on the system. Over the whole

cycle, an amount of heat Q_1 is taken in and $-Q_2$ is given out (the negative sign denotes that heat is lost by the system). The heat taken in by the system is therefore $Q_1 - (-Q_2) = Q_1 + Q_2$ and this is equal to the work done, W , by the system during the cycle. W is also equal to the net work done in the isothermal stages, *i.e.*

$$RT_1 \log_e \frac{V_3}{V_2} + RT_2 \log_e \frac{V_1}{V_4} \quad \dots \quad (2)$$

For an adiabatic change it can be shown that¹

$$\left(\frac{V_1}{V_2}\right)^{\gamma-1} = \frac{T_1}{T_2}, \text{ and } \left(\frac{V_4}{V_3}\right)^{\gamma-1} = \frac{T_1}{T_2}$$

where γ is the ratio of the specific heats of the gas at constant pressure

and at constant volume; $\gamma = \frac{C_p}{C_v}$.

$$\therefore \frac{V_4}{V_3} = \frac{V_1}{V_2}.$$

We may therefore substitute $\frac{V_2}{V_3}$ for $\frac{V_1}{V_4}$ in equation (2) above:

$$\therefore W = R(T_1 - T_2) \log_e \frac{V_3}{V_2}$$

$$\text{and } Q_1 = RT_1 \log_e \frac{V_3}{V_2}$$

$$\therefore \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1}.$$

¹ See Chapter, VII (§ 124).

and this is the efficiency of a process operating in a reversible cycle between temperature T_1 and T_2 .

The expression can also be written

$$\frac{Q_1 + Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}.$$

The result of this is that even in a reversible cycle (the most efficient type) not all the heat that goes into the cycle reappears as work. Some of it is lost as heat given out at the lower temperature.

Only if the lower temperature is absolute zero is all the heat taken in by the cycle utilised as work. In other words the second law limits the efficiency of heat engines. The absolute scale of temperature is based on this equation for the efficiency of a reversible cycle.

107. Entropy.—The equation $\frac{Q_1 + Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$ may be used to define three thermodynamic functions. As

$$\frac{Q_1 + Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

$$\text{then} \quad 1 + \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$\frac{Q_2}{Q_1} = -\frac{T_2}{T_1}$$

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0, \quad \text{or} \quad \Sigma \frac{Q}{T} = 0$$

Consider any reversible cycle and divide it into a number of Carnot cycles (see Fig. 60). Starting at A and going through all the cycles successively from A to B, it can be shown that all paths inside the figure cancel each other leaving only the zig-zag outer path. This zig-zag path approximates to the path ABA of the reversible cycle, and by making each Carnot cycle smaller and increasing their number it can be made to correspond more closely to ABA. The reversible cycle can, therefore, be regarded as being made up of an infinite number of Carnot's cycles. Now for each Carnot cycle the relation

$$\Sigma \frac{Q}{T} = 0 \text{ holds;}$$

so for an infinite number of Carnot cycles

$$\oint \frac{dQ}{T} = 0$$

(\oint Represents the integral around the cyclic path ABA.)

If the cycle is divided into two sections, then

$$\int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ}{T} = \oint \frac{dQ}{T} = 0$$

\int_A^B is the integral A to B along path α and \int_B^A is similarly defined.

Therefore $\int_A^B \frac{dQ}{T} = - \int_B^A \frac{dQ}{T} = \int_A^B \frac{dQ}{T}$

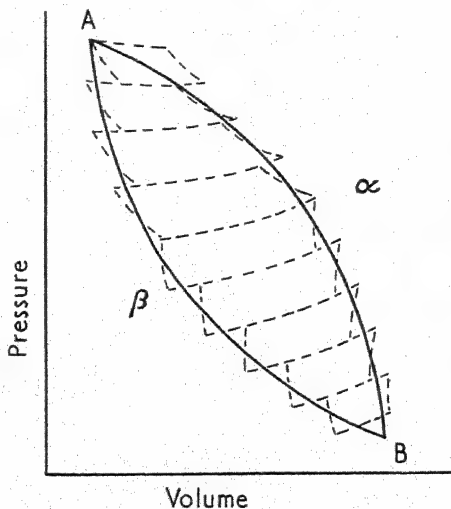


FIG. 60.

The continuous lines indicate that the system is brought from A to B by path α and back from B to A by path β . The dotted lines show the division of the cycle into a number of small Carnot cycles.

Both these integrals are therefore independent of the path taken from A to B. Both depend on the value of some function at A and the same function at B. Let this function be given the symbol S , then

$$\Delta S = S_B - S_A = \int_A^B \frac{dQ}{T}$$

$$\text{and } \frac{dQ}{T} = dS$$

S is a function known as *entropy*. Like U and H it is dependent only on the state of the system. That is, as stated above,

$$\Delta S = S_B - S_A$$

in any change from B to A whether the change is reversible or not, but

$$\Delta S = \int_A^B \frac{dQ}{T}$$

only applies when the change is a reversible one.

The change of entropy in a process is $\Sigma \frac{Q}{T}$ if the process is reversible:

hence this expression may be used to calculate entropy changes for reversible processes. For example in the fusion of solids the change in

entropy is given by $\frac{\Delta H_f}{T}$: where ΔH_f is the heat of fusion and T is

the melting point. Entropy is measured in entropy units which are calories per degree. Thus the change in entropy on the evaporation of 1 mole of water at 100°C. is the latent heat of evaporation of 1 mole of water (9,650 cal. per mole) divided by the absolute temperature 373°K. Therefore the change in entropy is

$$\frac{9,650}{373} = 25.7 \text{ cal./mole deg.}$$

In calculating the entropy change involved in the isothermal expansion of an ideal gas from V_1 to V_2 , use can be made of the fact that the heat absorbed is equal to the work done: hence

$$\begin{aligned} \Delta S = \frac{Q}{T} &= \frac{1}{T} \int_{V_1}^{V_2} P dV = \frac{RT}{T} \log_e \frac{V_2}{V_1} \\ &= R \log_e \frac{V_2}{V_1}. \end{aligned}$$

In the case of a non-isothermal change carried out at constant pressure

$$\Delta S = \int_{T_1}^{T_2} \frac{dQ}{T}.$$

Here T_1 and T_2 represent the initial and final temperatures. The heat absorbed $dQ = C_p dT$, where C_p is the molal heat capacity at constant pressure.

$$\text{Hence } \Delta S = \int_{T_1}^{T_2} \frac{C_p dT}{T}.$$

If C_p is constant over the temperature range T_1 to T_2 then

$$\Delta S = C_p \log_e \frac{T_2}{T_1}.$$

However, C_p does depend on temperature, and in order to evaluate the integral an empirical formula to express the relationship between C_p and T , or a graphical method is used. The latter is applied by writing

$$\int_{T_1}^{T_2} C_p \frac{dT}{T} \text{ as } \int_{T_1}^{T_2} C_p d(\log_e T), \text{ plotting } C_p \text{ as a function of } \log_e T \text{ and}$$

evaluating the area enclosed by the curve between T_1 and T_2 . In a non-isothermal change at constant volume, C_v replaces C_p in the above expressions.

$$\text{It should be noted that the expression } \Delta S = \int_{T_1}^{T_2} C_p d(\log_e T) \text{ applies}$$

to all systems and not only to those composed of ideal gases. The equations given may be applied to determine the difference in entropy of any substance at temperature T and at absolute zero. It is necessary to know the specific heats over the range of temperatures considered, the heat absorbed in any phase changes and the temperatures at which these changes occur. For example, to obtain the entropy difference between a substance in the gaseous phase at T° and the substance at 0°K the following equation would be used

$$S - S_0 = \int_0^{T_m} C_p d(\log_e T) + \frac{L_m}{T_m} + \int_{T_m}^{T_b} C_p d(\log_e T) + \frac{L_b}{T_b} + \int_{T_b}^T C_p d(\log_e T)$$

The integral from 0 to T_m represents the increase in entropy of the substance in the solid state while the temperature is being raised from 0 to T_m (the melting point); the integral from T_m to T_b the increase in entropy from T_m to T_b (the boiling point) and the integral from T_b to T is the increase from T_b to T where T is the temperature at which the value of the entropy is required. S_0 is the entropy at zero, L_m the latent heat of fusion and L_b the latent heat of evaporation. This equation assumes boiling and melting to be the only phase changes. The various integrals are evaluated graphically and the expressions L_m/T_m and L_b/T_b allow for the isothermal changes in entropy which occur at the phase changes of boiling and melting. C_p over the range of temperatures involved, the temperatures of the phase changes and the heat increases or decreases involved in these phase changes can all be determined experimentally.

The expression given for $S - S_0$ evaluates the entropy difference between 0°K and any required temperature. But it does not determine the absolute entropy S of a substance since the term S_0 remains:

this is an undetermined constant which is the entropy of the substance at absolute zero.

Nernst in considering how changes in the heat content and a function called the Gibb's free energy (§ 109) of a process varied with temperature, was led to advance what is called the Nernst Heat Theorem. This states that the change in entropy for a reaction involving crystalline solids at absolute zero is zero. The Nernst heat theorem was developed into the Third Law of Thermodynamics. This may be stated as follows: "*Every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero and does so in the case of a perfect crystalline solid.*"

The constant of integration S_0 given in the previous expression can now be stated to be zero using the third law of thermodynamics. Therefore the expression given to evaluate $S - S_0$ does actually give the absolute entropy of a substance because $S_0 = 0$ assuming the substance a perfect crystal at 0°K. A knowledge of entropy is of great importance. Entropy may also be calculated on the basis of statistical mechanics (§ 115).

108. Entropy Changes in Irreversible Processes.—The efficiency of an irreversible cycle is less than that of a reversible one. Hence for an irreversible cycle

$$\frac{Q_1^* + Q_2^*}{Q_1^*} < \frac{T_1 - T_2}{T_1}$$

(The asterisk is used to denote irreversible changes.)

This means that

$$\frac{Q_1^*}{T_1} + \frac{Q_2^*}{T_2} < 0$$

If one portion of a cycle is irreversible and the other reversible the cycle as a whole will be irreversible and the inequality

$$\frac{Q_1^*}{T_1} + \frac{Q_2}{T_2} < 0$$

will be valid.

Now consider a cycle in which the path from A to B is traversed irreversibly and the path from B to A reversibly. Then applying the previous inequality

$$\int_A^B \frac{dQ^*}{T} + \int_B^A \frac{dQ}{T} < 0$$

$$\int_B^A \frac{dQ}{T} = S_A - S_B$$

(because this part is reversible)

$$\therefore \int_A^B \frac{dQ^*}{T} < S_B - S_A.$$

In other words $\int_A^B \frac{dQ^*}{T}$ for an irreversible change does not give the

change in entropy but is equal to a quantity less than it.

When the system takes in heat, dQ , from its surroundings at T , the surroundings lose heat dQ at T reversibly, which is taken up by the system irreversibly. Then the decrease in the entropy of the sur-

roundings is given by $\int \frac{dQ}{T}$. If the heat is taken in irreversibly by the

system in going from state A to B then as has been seen

$$S_B - S_A < \int \frac{dQ}{T}.$$

But $\int \frac{dQ}{T}$ is the decrease in entropy of the surroundings, so the system

has gained more entropy than the surroundings have lost. Thus the irreversible process has been accompanied by an increase in the sum of the entropies of the surroundings and the system. As spontaneous processes are irreversible it has, therefore, been deduced that spontaneous processes are accompanied by an increase in the entropy of the system and surroundings. This is a very important deduction from the second law of thermodynamics. In fact Clausius has used this conception to state the second law as "The total amount of entropy in Nature is increasing".

109. The Free Energy Functions.—Up to this point three thermodynamic functions have been defined. It is now necessary to introduce two more functions: The Helmholtz free energy (F) and the Gibbs free energy (G). These are particular cases of a work function A and are defined by the relations:

$$F = U - TS \text{ and } G = H - TS.$$

The significance of these functions will now be explained. The efficiency of any reversible process working in a cycle between tem-

$$\text{peratures } T_1 \text{ and } T_2 \text{ is } E = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1}.$$

Assume a reversible isothermal cycle BCDE is described. Because the cycle is isothermal $T_1 = T_2$ and therefore $W = 0$. The work done

in going from B to D by C is equal to the work done in going D to B by E. As the paths have been chosen arbitrarily, the relation is independent of the path chosen. It follows that a work function A can now be defined. This is a function of the state of the system only. The value of A in a particular state is a measure of the work obtainable from the system in that state. The function A is such that when the system goes from state 1 to state 2 in an isothermal reversible manner the maximum work the system can do is given by the decrease in A , that is by $(A_2 - A_1) = -\Delta A$. (A negative sign is used because when work is done by the system the capacity of the system for work, i.e., A , decreases). The Helmholtz and Gibbs free energies are particular cases of the work function A .

If the isothermal reversible change is carried out at constant volume there is no mechanical work done against pressure. That is the whole decrease in A is available for work other than mechanical work; e.g., the work may be electrical. In such a case the symbol F is used for the work function and F must be so defined that the decrease in F , $-\Delta F$, measures the maximum work a system may do in an isothermal reversible change at constant volume.

If a change is carried out at constant pressure, P , it will in general have been accompanied by a volume change ΔV and hence the system will have done mechanical work $P\Delta V$. So the work, other than mechanical is $-\Delta F - P\Delta V$ and $-\Delta G = -(\Delta F + P\Delta V)$. It is important to stress that F and G like U , H and S are functions of the states of the system only. In any change ΔF and ΔG depend only the initial and final states: but the work (other than mechanical work) done is ΔF only if the change is an isothermal reversible one carried out at constant volume, and is ΔG only if the change is a reversible isothermal one carried at constant pressure.

F and G can now be expressed in terms of other functions. We start with the equation: $\Delta U = Q - W$. For a reversible isothermal change

$$\Delta S = \frac{Q}{T}; Q = T\Delta S. \text{ At constant volume } W = -\Delta F \text{ and hence}$$

$$\Delta U = T\Delta S + \Delta F \text{ or } \Delta F = \Delta U - T\Delta S. \text{ Hence } F = U - TS.$$

For a reversible isothermal change at constant pressure

$$W = -\Delta G + P\Delta V$$

$$\text{hence } \Delta U = T\Delta S + \Delta G - P\Delta V$$

$$\Delta G = \Delta U + P\Delta V - T\Delta S$$

$$\text{or } \Delta G = \Delta H - T\Delta S$$

$$\text{hence } G = H - TS$$

The expressions for ΔG and ΔF are most important; they are true for any change, reversible or not, because all the functions involved are

functions of the state of the system and depend only on the initial and final states of the system.

Starting with the equation

$$G = U + PV - TS \text{ and differentiating}$$

$$dG = dU + PdV + VdP - TdS - SdT.$$

But $dU = dQ - PdV$, and for a reversible change

$$dQ = TdS$$

$\therefore dG = VdP - SdT$; at constant pressure

$$dG = -SdT.$$

Consider a system in state 1; then

$$dG_1 = -S_1dT \text{ and in the state 2}$$

$$dG_2 = -S_2dT.$$

Subtracting dG_1 from dG_2 leads to

$$d(G_2 - G_1) = -(S_2 - S_1)dT \text{ and writing}$$

$$G_2 - G_1 = \Delta G \text{ and } S_2 - S_1 = \Delta S \text{ gives}$$

$$d(\Delta G) = -\Delta SdT$$

$$\therefore \left(\frac{\partial(\Delta G)}{\partial T} \right)_p = -\Delta S$$

Utilising the fact that ΔS is equal to $-\left(\frac{\partial(\Delta G)}{\partial T} \right)_p$ the relationship $\Delta G = \Delta H - T\Delta S$ can be written $\Delta G - \Delta H = T\left(\frac{\partial(\Delta G)}{\partial T} \right)_p$

This relationship is known as the Gibbs-Helmholtz equation.

150. Maxwell's Relationships.—From a consideration of the definitions given to the various thermodynamic functions a number of important relationships can be deduced.

Starting with $F = U - TS$ and differentiating

$$dF = dU - TdS - SdT$$

but $dU = dQ - PdV$; and in an isothermal reversible change $dQ = TdS$; so

$$dU = TdS - PdV, \text{ and substituting this expression}$$

for dU in the expression for dF , gives

$$dF = TdS - PdV - TdS - SdT.$$

$$\therefore dF = -PdV - SdT.$$

At constant temperature

$$\left(\frac{\partial F}{\partial V} \right)_T = -P \text{ and at constant volume } \left(\frac{\partial F}{\partial T} \right)_V = -S$$

Then $\frac{\partial^2 F}{\partial V \partial T} = - \left(\frac{\partial P}{\partial T} \right)_V$ and $\frac{\partial^2 F}{\partial T \partial V} = - \left(\frac{\partial S}{\partial V} \right)_T$

$$\therefore - \left(\frac{\partial P}{\partial T} \right)_V = - \left(\frac{\partial S}{\partial V} \right)_T \text{ or}$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T \quad (1)$$

Similar treatment of the expression

$dU = TdS - PdV$ gives the relationship

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad (2)$$

while treatment of the equation

$$dH = TdS + VdP$$

$$\text{gives } \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \quad (3)$$

and the equation $dG = VdP - SdT$

$$\text{gives } \left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T \quad (4)$$

These four relationships (1), (2), (3) and (4) between the partial derivatives are known as Maxwell's thermodynamic relationships.

111. Clapeyron-Clausius Equation.—This equation concerns the evaporation of a liquid, or the fusion of a solid. In the former process a system undergoing the change consists of one component and two phases; hence by the phase rule (see Chapter XI) there is only one degree of freedom.

The Maxwell relationship

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T \text{ is applied to the system. Because the}$$

system has only one degree of freedom we can replace

$$\left(\frac{\partial P}{\partial T} \right)_V \text{ by } \frac{dP}{dT}$$

(that is P depends on the temperature only and not on volume).

$$\left(\frac{\partial S}{\partial V} \right)_T \text{ can be replaced by } \left(\frac{\Delta S}{\Delta V} \right)_T$$

The change in entropy on evaporation is $\frac{l}{T}$ where l is the latent heat of evaporation and T the boiling point. The change in volume is $V - V_1$, V being the volume of vapour and V_1 the volume of liquid.

$$\therefore \left(\frac{\Delta S}{\Delta V} \right) T = \frac{l}{T(V - V_1)};$$

this gives $\frac{dP}{dT} = \frac{l}{T(V - V_1)},$

which is the Clapeyron-Clausius equation.

If the volume of liquid is neglected compared with that of the vapour,

$$l = T \frac{dP}{dT} V,$$

which can now be readily integrated, if it is supposed that l does not vary with temperature. This is only true over small temperature ranges.

The gas law states

$$V = \frac{RT}{MP}$$

$$\therefore l = \frac{RT^2}{MP} \cdot \frac{dP}{dT},$$

where M is the molecular weight. If $Ml = L$, the molecular latent heat, we have

$$L = \frac{RT^2}{P} \cdot \frac{dP}{dT}, \text{ or } \frac{dT}{T^2} = \frac{R}{L} \cdot \frac{dP}{P},$$

$$\log_e \frac{P_2}{P_1} = \frac{L}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

where P_1 and P_2 are the vapour pressures at T_1 and T_2 .

Throughout the above, it has been assumed that the vapour acts as a perfect gas.

Elevation of Boiling Point.—The Clapeyron-Clausius equation may be used to obtain the molecular elevation from the latent heat. If there is an elevation δT when w gms. of a solute are dissolved in 100 gms. of solvent, and M is the molecular weight of the solute, the molecular elevation, k , is given by the equation

$$k = \frac{M\delta T}{w}, \quad \cdot \quad \cdot \quad \cdot$$

If the boiling point of the pure solvent is T , and that of the solution $T + \delta T$ when the atmospheric pressure is P_1 , then

P_1 is the vapour pressure of the solution at $T + \delta T$ and is also the vapour pressure of the solvent at T , and

P_2 is the vapour pressure of the solvent at $T + \delta T$.

P_2 may be calculated from the Clapeyron-Clausius equation, since

$$\log_e \frac{P_2}{P_1} = \frac{L}{R} \left\{ \frac{1}{T} - \frac{1}{T + \delta T} \right\} \cdot$$

$$\begin{aligned}
 &= \frac{L}{R} \frac{\delta T}{T(T + \delta T)}, \\
 &= \frac{L\delta T}{RT^2}, \text{ when } \delta T \text{ is very small.}
 \end{aligned}$$

Now $\log_e \frac{P_2}{P_1} = \log_e \left(1 + \frac{P_2 - P_1}{P_1} \right) = \frac{P_2 - P_1}{P_1}$, the remainder of the terms being neglected, since $P_2 - P_1$ will be small.

By Raoult's Law, $\frac{P_2 - P_1}{P_2} = \frac{n}{N}$, where n = number of molecules of solute and N = that of solvent. When the difference between P_2 and P_1 is very small, as has just been supposed, $\frac{P_2 - P_1}{P_2}$ may be taken to be equal to $\frac{P_2 - P_1}{P_1}$;

$$\therefore \frac{n}{N} = \frac{L\delta T}{RT^2}.$$

But $n = \frac{w N_0}{M}$, and $N = \frac{100 N_0}{M'}$, where M is the molecular weight of solute, M' is the molecular weight of solvent, and N_0 is Avogadro's Number.

$$\begin{aligned}
 \therefore \frac{wM'}{100M} &= \frac{L\delta T}{RT^2}, \\
 \delta T &= \frac{RT^2 w M'}{100 M L}.
 \end{aligned}$$

$$\text{Hence, } k = \frac{M\delta T}{w} = \frac{M}{w} \cdot \frac{RT^2 w M'}{100 M L} = \frac{M'}{L} \cdot \frac{RT^2}{100}.$$

But

$$\begin{aligned}
 L/M' &= l, \\
 \therefore k &= \frac{RT^2}{100l}.
 \end{aligned}$$

Putting $R = 2$ gm.-cals., we have

$$k = \frac{0.02T^2}{l}.$$

Depression of the Freezing Point.—A similar calculation gives the expression

$$k = \frac{0.02T^2}{l}$$

for the molecular depression of the freezing point, where l is now the latent heat of fusion.

112. Equilibrium.—While a system is in equilibrium the only changes it can undergo are reversible ones. This is because being already at equilibrium it cannot undergo a natural process; nor can it

move away from equilibrium for that would be an unnatural process; hence the only process possible is a reversible one. On the basis of thermodynamics we can write down the criteria for reversible processes, and these then give the conditions for equilibrium. In this treatment it is assumed that the only type of work that can be done by the system is the type involved in changing the volume, that is mechanical work.

For an adiabatic change $Q = 0$. (Q is the heat taken in by the system.) If the change is reversible $dS = \frac{Q}{T}$; so for a reversible adiabatic change $dS = 0$.

In any process $dU = Q - W$. Therefore in an adiabatic process $dU = -W$. At constant volume $W = 0$ so $dU = 0$.

At constant pressure $W = PdV$ and $dU = -PdV$ and hence $dU + PdV = 0$, that is $dH = 0$.

For isothermal processes $dT = 0$. For a reversible process $dS = \frac{Q}{T}$ and so $Q = TdS$. Hence $dU = TdS - W$. At constant volume $W = 0$ so $dU - TdS = 0$. That is $dF = 0$. At constant pressure $W = PdV$ so $dU = TdS - PdV$; that is $dU - TdS + PdV = 0$, so $dG = 0$.

The conditions for reversibility may now be summed up. Adiabatic changes $Q = 0 \therefore dS = 0$.

At constant volume, $dS = 0, dV = 0, dU = 0$;

at constant pressure, $dS = 0, dP = 0, dH = 0$.

Isothermal changes, $dT = 0$.

At constant volume, $dT = 0, dV = 0, dF = 0$;

at constant pressure, $dT = 0, dP = 0, dG = 0$.

Therefore, if a reversible change takes place at constant volume and constant internal energy the entropy is constant; at constant pressure and constant entropy the heat content is constant; at constant temperature and volume the Helmholtz free energy is constant and at constant temperature and pressure the Gibbs free energy is constant.

As we explained at the beginning of this section these are also conditions for equilibrium. However, the terms $dS = 0, dH = 0, dF = 0$ and $dG = 0$ can mean that the functions, S, H, F and G are either a maximum or a minimum. As shown in a previous paragraph entropy in spontaneous processes tends to increase; therefore, the state of maximum entropy corresponds to a state of stable equilibrium, and minimum entropy to a state of unstable equilibrium.

It can also be shown that for H, G and F the state of stable equilibrium is the state of minimum value of these functions. Thus, summing up, the conditions for stable equilibrium are:

T and P constant, G is a minimum;

T and V constant, F is a minimum;

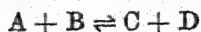
S and P constant, H is a minimum;

U and V constant, S is a maximum.

This means that a process taking place at constant temperature and pressure will proceed until the system reaches a state of minimum G . In other words natural processes take place with decrease of G . The decrease in free energy accompanying a chemical reaction is sometimes called the affinity of the reaction. Similarly natural processes take place with increase of entropy.

113. Law of Mass Action Thermodynamically.—The law of Mass Action (see § 196) can be deduced thermodynamically by using the so-called van't Hoff equilibrium box.

The "equilibrium box" is a theoretical device by which the reaction



can be made to take place by a series of reversible operations. It is supposed to have one wall permeable to A , another to B , another to C and another to D .

It is supposed, for the sake of simplicity, that the reactants and products are perfect gases. Let p_a and p_b be the initial pressures of A and B . The equilibrium pressures are P_A , P_B , P_C and P_D . The final pressures of C and D are p_c and p_d .

The reversible operations are:

(1) Alter the pressure on A from the initial to the equilibrium pressure. The work done by the gas is

$$\int_{P_A}^{p_a} v dp = RT \log_e \frac{p_a}{P_A}.$$

(2) Do the same with B , the work done by the gas being

$$\int_{P_B}^{p_b} v dp = RT \log_e \frac{p_b}{P_B}.$$

(3) Introduce 1 gm. molecule of the gas A and 1 gm. molecule of the gas B through their respective semi-permeable walls into the equilibrium box. The four gases A , B , C and D are already present in the box as an equilibrium mixture at their equilibrium partial pressures P_A , P_B , P_C and P_D . The introduction of A and B will not involve any work being done as the partial pressures of A and B inside the box are equal to the pressures of the gases entering the box. A and B now react to produce 1 gm. molecule of C and D . It is assumed that the volume of the box is so large that these operations cause no appreciable change in the composition of reactants within the box.

(4) One gm. molecule of C and D are now removed from the box through their respective walls. The pressures of C and D are not changed during this removal so no work is done.

(5) They are reduced to the final pressures. The work done by the gases in this process is, by C,

$$\int_{p_c}^{P_c} v dp = RT \log_e \frac{P_c}{p_c},$$

$$\text{and by D, } RT \log_e \frac{P_D}{p_d}.$$

The change in free energy is equal to the total work which has been performed by the gases; hence

$$-\Delta G = RT \log_e \frac{p_a}{P_A} + RT \log_e \frac{p_b}{P_B} + RT \log_e \frac{P_c}{p_c} + RT \log_e \frac{P_D}{p_d}.$$

$$-\Delta G = RT \log_e \frac{P_D P_C}{P_A P_B} - RT \log_e \frac{p_d p_c}{p_a p_b}.$$

The change in free energy depends only on the initial and final states. That is $-\Delta G$ is not affected by the partial pressure in the equilibrium box. Hence the first term of the right-hand side must be a constant at any given temperature, that is $RT \log_e \frac{P_C P_D}{P_A P_B}$ is constant;

therefore $\frac{P_C P_D}{P_A P_B} = \text{constant } K_p$, the equilibrium constant.

Here the equilibrium constant is expressed in terms of partial pressures. The deduction can also be carried out in terms of concentration and this will give $\frac{C_D C_C}{C_A C_B}$ (all at equilibrium) = K_c .

If we start with each reactant at a partial pressure of one atmosphere and end with each product at partial pressure of one atmosphere then the second term in the right-hand side of the ΔG equation will disappear and

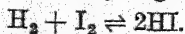
$$-\Delta G = RT \log_e K_p.$$

This quantity is known as the standard free energy change usually symbolised by ΔG° .

The treatment can be generalised to a reaction of the type $N_1 A_1 + N_2 A_2 + \dots \rightleftharpoons N_1' A_1' + N_2' A_2' + \dots$ and

$$-\Delta G = RT \log_e K_p - RT \log_e \frac{[A_1']^{N_1'} [A_2']^{N_2'} \dots}{[A_1]^{N_1} [A_2]^{N_2} \dots}.$$

This is generally known as the van't Hoff isotherm. As an example of the use of the van't Hoff isotherm, the affinity of hydrogen for iodine when they combine to give hydrogen iodide may be calculated.



According to Bodenstein, at 443° C., $K = 50.62$.

Hence,

$$-\Delta G = RT \log_e K = 2 \times 716 \times 2.303 \times \log_{10} 50.62 = 5,619 \text{ gm.-cals.}$$

Since there is no change in pressure as a result of the reaction, the second term of the isotherm disappears.

At 500° C., $K = 41$, hence

$$-\Delta G = RT \log_e K = 2 \times 773 \times 2.303 \log_{10} 41 = 5,760 \text{ gm.-cals.}$$

114. The van't Hoff Isochore.—The Gibbs-Helmholtz equation gives:

$$\Delta G - \Delta H = T \left(\frac{\delta (\Delta G)}{\delta T} \right)_p$$

Rearrangement of this leads to:

$$\Delta H = \Delta G - T \left(\frac{\delta (\Delta G)}{\delta T} \right)_p$$

Dividing by T^2 gives

$$\frac{\Delta H}{T^2} = \frac{\Delta G - T \left(\frac{\delta (\Delta G)}{\delta T} \right)_p}{T^2}$$

Now $-\frac{d \left(\frac{\Delta G}{T} \right)_p}{dT}$ gives the right-hand side of the equation;

$$\text{so } \frac{\Delta H}{T^2} = - \frac{d \left(\frac{\Delta G}{T} \right)_p}{dT}$$

If this is applied to a free energy change which involves only the standard free energy change, ΔG may be replaced by ΔG° which in turn may be replaced by $-RT \log_e K_p$, giving

$$\frac{\Delta H}{T^2} = \frac{R d(\log_e K_p)}{dT}$$

that is $\frac{d}{dT} \log_e K_p = \frac{\Delta H}{RT^2}$ where ΔH is the heat of reaction absorbed at constant pressure. This relation is known as the van't Hoff isochore.

In applying the van't Hoff isochore to any particular case, it is necessary to integrate the expression, which cannot be used as it stands. The problem, then, is to integrate the equation

$$\frac{d}{dT} \log_e K_p = \frac{\Delta H}{RT^2}$$

It is necessary first of all to make an assumption concerning ΔH , i.e., that it is independent of temperature over a small range. Practically,

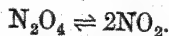
this is not quite true, but sufficiently nearly so to enable the calculation to be made, and the result applied with fair accuracy.

We have then

$$\int_{K_{P_1}}^{K_{P_2}} d(\log_e K_p) = \int_{T_1}^{T_2} \frac{\Delta H \cdot dT}{RT^2},$$

$$\log_e \frac{K_{P_2}}{K_{P_1}} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = -\frac{\Delta H}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right).$$

As an example of the use of this equation, we may take the dissociation of nitrogen tetroxide,



The equilibrium constant of this reaction $\left(\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \right)$ is 0.0017 at 27° C.

and 1 atmosphere. At 111° C. the equilibrium constant is 0.204. It is required to calculate the heat of dissociation per gram-molecule.

We first of all convert the isochore into logarithms to the base 10, and then substitute the values given.

$$\log_{10} \frac{K_{P_2}}{K_{P_1}} = \frac{-\Delta H}{2.303 R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

$$K_{P_2} = 0.0017, \quad T_2 = 27 + 273 = 300^\circ \text{ Abs.}$$

$$K_{P_1} = 0.204, \quad T_1 = 111 + 273 = 384^\circ \text{ Abs.}$$

$$R = 1.987 \text{ gm.-cals. per degree}$$

$$\therefore \log_{10} \frac{0.0017}{0.204} = \frac{-\Delta H}{4.576} \left(\frac{84}{300 \times 384} \right)$$

$$\therefore \Delta H = + 13,100 \text{ gm.-cals.}$$

Hence, the heat absorbed per gram-molecule is 13,100 gm.-cals. A further example is given in Chapter X. (§ 202).

In order to carry out the integration of the van't Hoff isochore accurately it is necessary to express ΔH as a function of temperature.

115. The Statistical Nature of the Second Law.—It has been said previously that the second law states that spontaneous processes are irreversible; as an example of this it was pointed out that gases in a compartment do not build up regions of varying pressure; the molecules of the gas are uniformly distributed through the box. Further as the system is in equilibrium the entropy is a maximum.

A gas is made up of molecules which are moving in a completely random fashion. It is conceivable that if all the gas molecules started moving at the same time in the same direction that the uniform distribution of the molecules would be upset. That is there could be a region in the box in which the density of molecules is greater than the density of molecules in rest of the box. In this type of process (a spontaneous

process) the uniform distribution of molecules in the box has been reversed and the second law violated; but it is obvious that the probability against such a reversal taking place is enormous. It would involve a large number of independent molecules all starting to move in the same direction at the same time. It can be seen that though the second law can be broken, the probability against it being broken is very large. The movement of the molecules is disordered and the probability of ordered movement is very small. Equilibrium is a state of maximum disorder. Equilibrium is also the state of maximum entropy. Entropy can therefore be associated with the disorder of a state.

Consider a large number of molecules making up a mass of gas which has definite bulk properties, such as pressure and volume, there are very many arrangements of the molecules that can give the required bulk properties. The molecules can differ enormously in their behaviour and still give the bulk properties of the state. Each arrangement of the velocities and positions of the molecules which gives the required bulk properties is called a micro-state. The number of micro-states associated with a particular bulk state is defined as the thermodynamic probability, W , of that state. It is postulated that all micro-states are equally probable. In attaining equilibrium a system moves to the state of maximum probability.

A relationship between entropy and thermodynamic probability can be derived by considering a system consisting of two masses of gas separated by a partition. The entropy of one of the masses is S_1 and the probability is W_1 ; and the entropy and probability of the other are S_2 and W_2 . If the partition is removed, the entropy of the complete system is $S_1 + S_2$ while the probability is $W_1 W_2$. Any relationship between entropy and probability must be such that while the entropy is additive the probability must be multiplicative. A relation of this type: $S = \text{Constant} \log_e W + \text{constant}$, will satisfy the required condition. Planck postulated that the second constant is zero and that the relation is $S = k \log_e W$. It can be shown that k is the gas constant per molecule,¹ $\frac{R}{N}$ where N is the Avogadro number. This equation is the

basis of statistical thermodynamics.

The thermodynamic probability relates to the number of ways in which molecules can be distributed with respect to energy. According to the classical theory energy was continuous and a molecule could have any energy; in quantum theory only certain values of the energy are allowed. There is one distribution of molecules among the allowed energies that is more probable than any other distribution. When dealing with a very large number of molecules the probability of any distribution other than the most probable becomes very small; the

¹ k is called the Boltzmann Constant.

molecules may then be regarded as being distributed according to the most probable distribution. The most probable distribution calculated by classical mechanics is $N_i = N_0 e^{-E_i/kT}$ where N_i is the number of molecules in the i th energy level, E_i being the energy of molecules in that level; N_0 is the number of molecules in the lowest level and T the temperature of the system. This distribution is known as the Maxwell Boltzman distribution. The Maxwell-Boltzman distribution is derived on a number of assumptions which are not valid in quantum theory. However, the distributions derived on the basis of quantum mechanics differ appreciably from the classical distribution only at low temperatures and high pressures; the classical distribution may be used in problems which do not involve these conditions.

It can be shown also that $N_i = \frac{N e^{-E_i/kT}}{Q}$ where N is the total number of molecules in a system and $Q = \sum_i e^{-E_i/kT}$. Q is called the

partition function. All the thermodynamic functions can be expressed as functions of Q and hence the evaluation of Q makes it possible to calculate such quantities as G , S , U and F . For S the calculation is based on the postulate $S = k \log_e W$ and entropies calculated in this way agree in most cases with those evaluated on the basis of the third law of thermodynamics; such discrepancies as do occur can be explained, but the explanations introduce conceptions too advanced for this book.

The calculation of Q is usually carried out on the assumption that the various types of energy¹ (e.g., rotational, translational, and vibrational) do not interact and can be treated separately; the energy is written $E_i = E_r + E_t + E_v + E_n + E_e$ where E_r is the rotational energy of the molecule, E_t the translational energy, E_v the vibrational energy, E_n the nuclear spin energy (see § 65) and E_e the electronic energy.

The partition function Q can then be written

$$\begin{aligned} Q &= \sum_i e^{-\frac{E_r + E_t + E_v + E_n + E_e}{kT}} \\ &= \sum_r e^{-E_r/kT} \sum_t e^{-E_t/kT} \sum_v e^{-E_v/kT} \sum_n e^{-E_n/kT} \sum_e e^{-E_e/kT} \\ &= Q_r \quad Q_t \quad Q_v \quad Q_n \quad Q_e \end{aligned}$$

The partition function is the product of the individual partition functions for each form of energy. Statistical mechanics only gives the distribution of the particles among allowed energy levels. The levels are calculated by the methods of quantum mechanics.

The calculation of the translational partition of a gas molecule in a rectangular box may be taken as an example. For such a molecule the

¹ See (§ 123).

potential energy $V = 0$. Substituting this value in the general Schroedinger equation gives the wave equation.

$$\nabla^2 \Psi + \frac{8\pi^2 m E \Psi}{h^2} = 0$$

The solution of this equation shows that the energy levels available for the gas molecules are quantised and are equal to

$$\frac{h^2}{8m} \left(\frac{p^2}{a^2} + \frac{q^2}{b^2} + \frac{r^2}{c^2} \right)$$

where a , b and c are the dimensions of the rectangular box, which contains the molecule, m is the mass of the molecule and p , q and r are quantum numbers.

Considering the movement of the molecule in one direction, say the x direction along the a dimension, then

$$E_x = \frac{h^2 p^2}{8ma^2};$$

so the translational partition function for the x direction is

$$Q_x = \sum_{p=0}^{\infty} e^{-h^2 p^2 / 8ma^2 kT}$$

The translational energy levels are very close together so the sum can be replaced by an integral;

$$Q_x = \int_0^{\infty} e^{-p^2 h^2 / 8ma^2 kT} dp$$

The evaluation of this integral gives $Q_x = \frac{(2\pi mkT)^{1/2} a}{h}$

Similar results are obtained for the other two dimensions, y and z .

$$\begin{aligned} \text{So } Q_t &= \frac{(2\pi mkT)^{3/2} abc}{h^3} \\ &= \frac{(2\pi mkT)^{3/2} V}{h^3} \end{aligned}$$

where V is the volume of the box. All the quantities in the last expression can be determined experimentally and, therefore, Q can be calculated. The evaluation of the partition functions of the other forms of energy involves the use of spectroscopic measurements.

SUGGESTIONS FOR FURTHER READING

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CHAPTER VII

GASES

116. The Kinetic Theory of Gases, and its Assumptions.—There is no clear dividing line between the solid and liquid state, or between the liquid and gaseous state. It is difficult to say where the one state ends and the other begins. Assuming that matter is made up of molecules, it is possible to say that in a gas the molecules have much greater freedom of motion than in either the solid or liquid state. They can move about much more easily, and can traverse greater distances without coming into collision with other molecules. This must be the case because of the pressure-volume relationships of a gas. When the pressure on a gas is doubled, the volume of the gas is reduced to one-half its previous value. Since this is possible, there must be a great deal of empty space in a gas. When the pressure on a liquid is doubled there is hardly any effect on the volume, and the same applies to a solid. In these states, then, the molecules must be much closer together than in a gas. As mentioned above, it cannot be too strongly emphasised that the three states of matter are continuous.

A gas may be defined as a substance which remains homogeneous, and of which the volume increases without limit, when the pressure on it is continuously reduced, the temperature being maintained constant.

The properties of a gas can be studied theoretically by making use of the kinetic theory of gases. In using this theory it must be remembered that certain assumptions are made which cannot be regarded as strictly correct. The theory was put forward before the structure of matter was understood, but nevertheless it has been extremely useful in explaining the properties of gases, and giving quantitative expressions of their behaviour.

The kinetic theory assumes that a gas is made up of particles; these correspond to the molecules of the atomic theory. The particles are moving in a random fashion having neither directional preference nor the same velocities. The theory further assumes that the molecules are solid, spherical and perfectly elastic; this is principally to make the mathematical calculations tractable.

According to the theory, the pressure exerted by a gas is due to the bombardment of the walls of the containing vessel by the molecules. Whenever a collision with the walls takes place a certain amount of momentum is given up to the walls, and this change of momentum, of course, is associated with a force. Obviously, the collisions between

molecules themselves, and between the molecules and the walls will be greater in number when the volume is decreased, for then there is less room for motion. Thus, the pressure is increased. *The average distance traversed by a molecule between one collision and the next is called the "mean free path".*

Heat is a form of energy, and when a gas is heated energy is imparted to it. It has been shown by studying the Brownian movement in gases (see Colloids, Chapter XVII.) that the mean kinetic energy of the molecules of a perfect gas (§ 118) depends only on the temperature, and not on the nature of the gas. This is of importance in studying the effect of temperature on pressure and volume of a gas.

With the aid of the assumptions made above, which must always be borne in mind, a number of laws governing the behaviour of gases can be derived.

117. Boyle's Law.—In order to carry out any calculations it is necessary first to realise that in a gas there is a great number of molecules, moving about with random motion, and with widely varying velocities. It would, of course, be impossible to work with conditions of this kind, so it is necessary to take an average value for the velocity. The ordinary average is not taken, but the molecules are given a velocity u , which, if they all possessed it, would make the value of the total kinetic energy, $\frac{1}{2}mnu^2$, actually what it is. In this expression m is the mass of one molecule, and n the number of molecules. This velocity u , is such that its square is equal to the mean of the squares of all the velocities possessed by the molecules, and is called the root-mean-square velocity.

Even now, we have to contend with the fact that the actual direction of motion of each molecule is not known; but use can be made of the fact that every velocity can be resolved into three velocities at right angles, governed by the relationship,

$$u^2 = u_x^2 + u_y^2 + u_z^2,$$

where u_x , u_y , u_z , are the three components, parallel respectively to the x , y and z axes (Fig. 61).

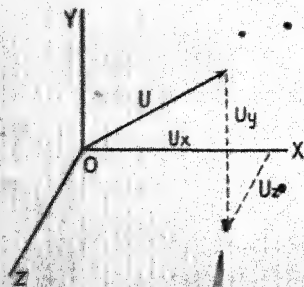


FIG. 61.

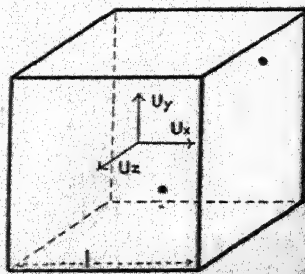


FIG. 62.

Now, consider a cube (Fig. 62) of side l , containing n molecules, each of mass m .

Consider one molecule in the cube. It has a root mean square velocity u , which can be resolved into three components mutually at right angles, and parallel to the edges of the cube, u_x, u_y, u_z . Consider the velocity u_x . The molecule may be supposed to be moving towards the right-hand wall. It possesses momentum mu_x when it reaches it, and since it is perfectly elastic, and the walls of the vessel are supposed to be so too, it rebounds with velocity $-u_x$, and momentum $-mu_x$.

The change in momentum is $2mu_x$. This occurs $\frac{u_x}{l}$ times per second. Hence the change in momentum for this particular component is $\frac{2mu_x^2}{l}$ per second.

Considering now the u_y component, we have, as before, the change of momentum per second $= \frac{2mu_y^2}{l}$.

Similarly for the u_z component. Hence the total change of momentum per second for all three components is

$$\frac{2mu_x^2}{l} + \frac{2mu_y^2}{l} + \frac{2mu_z^2}{l} = \frac{2mu^2}{l},$$

and, since force is measured by rate of change of momentum, this is equal to the total force over the surface of the cube.

Hence, force per unit area, i.e., the pressure exerted by each molecule is given by

$$p = \frac{2mu^2}{6l^3}.$$

For the total n molecules contained in the cube, the pressure is

$$p = \frac{2mnu^2}{6l^3} = \frac{1}{3} \frac{mnu^2}{l^3}.$$

If v is the volume of the cube, $v = l^3$, and

$$pv = \frac{1}{3} mnu^2 \quad \dots \quad (1)$$

At a given temperature, all the quantities on the right-hand side of this equation are constant. Hence $pv = \text{constant}$.

This is Boyle's Law, which has been proved theoretically, by making the assumptions of the kinetic theory. Boyle's Law, however, is not followed perfectly by any gas. Since the theory indicates that it *should* be true, it is obvious that something is wrong with the theory. This inaccuracy is to be found in the assumptions made, and will be dealt with later (§§ 126, 127).

118. Charles's or Gay-Lussac's Law.—It has been proved experimentally that the mean kinetic energy of the molecules of all gases is the same at the same temperature. This conclusion is also reached theoretically. Since no particular temperature need be specified, it follows that the rate of change of the kinetic energy with temperature is the same for all gases. Expressed mathematically,

$$\frac{d(\frac{1}{2}mu^2)}{dT} = \text{const.} \quad (2)$$

Equation (1) may be written

$$pv = \frac{2}{3}n(\frac{1}{2}mu^2),$$

which on differentiation with respect to T gives

$$\frac{d(pv)}{dT} = \frac{2}{3}n \left(\frac{d(\frac{1}{2}mu^2)}{dT} \right) + \frac{2}{3}(\frac{1}{2}mu^2) \left(\frac{dn}{dT} \right).$$

Substituting from equation (2), we have

$$\frac{d(pv)}{dT} = n \times \text{const.} + \frac{2}{3}(\frac{1}{2}mu^2) \frac{dn}{dT}.$$

If n is constant with respect to T —and this is true except for gases of which the molecular complexity varies with temperature—

$$\frac{d(pv)}{dT} = \text{const.}$$

In other words, the rate of change of the product of pressure and volume with the absolute temperature is constant; or, if pressure is constant, the rate of change of volume with absolute temperature is constant. This is Charles's Law, sometimes known as Gay-Lussac's Law.

119. Avogadro's Hypothesis.—We can write equation (1) in the form

$$n = \frac{3}{2} \frac{pv}{(\frac{1}{2}mu^2)}.$$

Hence, if for a number of samples of gases p , v and $\frac{1}{2}mu^2$ are constant, then n must be constant for them all.

Thus Avogadro's Hypothesis, which states that equal volumes (v constant) of gases, under the same conditions of temperature ($\frac{1}{2}mu^2$ constant) and pressure (p constant), contain the same number of molecules, has a theoretical basis in the kinetic theory. Since the assumptions of the kinetic theory are not strictly accurate, Avogadro's Hypothesis is not strictly true. The method of employing it in the determination of molecular weights from gaseous densities will be discussed later (§ 128).

120. Graham's Law of Diffusion.—Graham found that a light gas would diffuse through a porous diaphragm more rapidly than a heavy gas, and also found the quantitative law governing the diffusion, which states that the rate of diffusion of a gas is inversely proportional to the

square root of its density. This law can be shown to be justified on the basis of the kinetic theory.

We can rewrite equation (1) in the form

$$u^2 = \frac{3pv}{nm}$$

Now, the density of a gas = $\frac{nm}{v} = d$ (say).

$$\text{Thus } u^2 = \frac{3p}{d}; u = \sqrt{\frac{3p}{d}} \quad (3)$$

The reason why the light gas diffuses more rapidly through a porous diaphragm than the heavy gas has nothing to do with the size of the molecules as such. The pore of the diaphragm is, in any case, considerably larger in diameter than the largest molecule, and molecules, of whatever size, would find no difficulty in getting through. If the pore is magnified to the size of a railway tunnel, the large and small molecules might be represented by a bird and a bee respectively. Neither would have difficulty in traversing the tunnel.

The diffusion of the molecules of a gas through a porous membrane will depend upon the velocity of the molecules, and will be directly proportional to this. Hence,

$$r = ku = k \sqrt{\frac{3p}{d}} = k_1 \sqrt{\frac{1}{d}}$$

where k and k_1 are constants. This accounts for Graham's Law of Diffusion.

121. Molecular Velocities.—Equation (3) can be used directly for calculating the velocity of a molecule of any given gas. Of course, the value obtained will be the root-mean-square velocity, and not necessarily the velocity of any particular particles. It is interesting to calculate some of these velocities in order to gain an idea of the rate at which molecules move in gases. To do this, it must be remembered that if the velocities are to be found in c.g.s.u., i.e., in cm. per sec., the pressure and density must also be expressed in c.g.s.u.

To calculate the root mean square velocity of the molecules of hydrogen at atmospheric pressure.

$$u = \sqrt{\frac{3p}{d}}$$

$$d = 0.00009 \text{ gm. per c.c.}$$

$$p = 76 \times 13.59 \times 981 \text{ dynes per sq. cm.}$$

$$\begin{aligned} u &= \sqrt{\frac{3 \times 76 \times 13.59 \times 981}{0.00009}} \\ &= 183,800 \text{ cms. per sec.} \\ &\text{or } 1,838 \text{ m. per sec.} \end{aligned}$$

LIST OF MOLECULAR ROOT MEAN SQUARE VELOCITIES
AT N.T.P.

Hydrogen	1,838 metres per sec.
Oxygen	460 " "
Nitrogen	493 " "
Argon	410 " "
Water vapour	610 " "
Carbon dioxide	390 " "
Mercury vapour	180 " "

122. The Gas Constant.—In text-books on heat it is shown that by combination of the laws of Boyle and Charles, a general gas equation is arrived at of the form

$$pv = kT,$$

where k is a constant for the gas, and the other symbols have their usual significance; k , of course, will vary with the amount of gas considered. One gram-molecule of all gases under the same conditions of temperature and pressure occupies the same volume, so the value of k will be the same for all gases if, in every instance, one gram-molecule of the gas is considered. When this is done, k is replaced by R , and the general gas equation becomes

$$pv = RT$$

R may now be calculated. The value of R will vary according to the system of units used. If p is expressed in atmospheres, and v in litres, we obtain, as the calculation below shows, the value 0.08204 litre-atmospheres per degree.

$$p = 1 \text{ atmos.}, v = 22.4 \text{ litres}, T = 273^\circ \text{ Abs.}$$

$$\therefore R = pv/T = 22.4/273 = 0.08204 \text{ litre-atmos. per degree.}$$

If, however, p is expressed in dynes per sq. cm., and v in c.c., we obtain the value 8.314×10^7 ergs per degree, or 8.314 joules per degree¹ for R . This is derived as follows:—

$$p = 76 \times 13.596 \times 981 \text{ dynes per sq. cm.}, v = 22,414 \text{ c.c.},$$

$$T = 273.16^\circ \text{ Abs.}$$

$$R = pv/T = \frac{76 \times 13.596 \times 981 \times 22,414}{273.16}$$

$$= 8.314 \times 10^7 \text{ ergs per degree}$$

$$= 8.314 \text{ joules per degree.}$$

¹ *Note on Units.*—The *dyne* is the force which, acting on 1 gm., produces an acceleration of 1 cm. per sec. per sec. The *erg* is the amount of work done when a body, acted upon by a force of one dyne, moves through a distance of 1 cm. in the direction of the force. One *joule* equals 10^7 ergs. The *gram-calorie* is the amount of heat required to raise the temperature of 1 gm. of water by 1°C . Determinations of the mechanical equivalent of heat show that 1 gram-calorie is equivalent to 4.185×10^7 ergs.

Since 4.185×10^7 ergs = 1 gm.-calorie, $R = 1.99$ gm.-cals. per degree, or nearly 2 gm.-cals. per degree. The last is the value most frequently used in calculations.

123. The Specific Heats of Gases.—*The specific heat of a substance is the ratio of the amount of heat required to raise the temperature of 1 gm. of it through 1°C. , to that required to raise the temperature of 1 gm. of water through the same temperature range.*

It is a well-known fact that a substance has two specific heats, one measured at constant pressure, and one at constant volume. For a solid or a liquid the difference between the two is usually negligible, since the effect of heat on the volume is small. But, in the case of a gas, the expansion which takes place on heating is large, and consequently the two values of the specific heat are widely different. It is our purpose to calculate the ratio of the two specific heats for gases.

The kinetic energy of a gas molecule is proportional to its absolute temperature. From the equations

$$pv = RT$$

and

$$pv = \frac{1}{3} mnu^2,$$

it is clear that the kinetic energy per gram-molecule of a gas ($\frac{1}{2}mnu^2$) is $\frac{3}{2}RT$.

Thus, when a gram-molecule of a gas is heated from a temperature T to a temperature $T + 1$, the increase in kinetic energy is $\frac{3}{2}R = 3$ gm.-cals.

Thus, the molecular heat of a gas at constant volume is 3 gm.-cals., the definition of *molecular heat* being the amount of heat required to raise the temperature of one gram-molecule of a substance through 1°C. Note that this applies to any gas, and consequently the molecular heat of all gases at constant volume should be the same and equal to 3 gm.-cals.

In the case of diatomic and polyatomic molecules there are many other modes of distributing the energy besides simply as energy of translation. Some of the energy may be used in causing rotation or vibration. Thus, in raising the temperature of a gas of which the molecule is complex through the same temperature range as a simple gas, more energy will have to be imparted, and the molecular heat of the gas at constant volume will then be $3 + x$ gm.-cals., where x is an unknown increase in the energy and varies from gas to gas.

If the specific heat of a gas is measured at constant pressure instead of at constant volume, a different value will be found. Suppose 1 gm. of gas is heated from 0°C. to 1°C. , the volume being kept constant. The amount of heat imparted is the specific heat of the gas at constant volume. The operation may be supposed to take place in a vessel closed by a piston, the piston being kept fixed (Fig. 63).

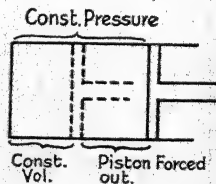


FIG. 63.

If now, in this apparatus, there is 1 gm. of gas at 0°C. , and it is heated to 1°C. , the piston being free, the piston will be forced out against the pressure of the atmosphere. The amount of heat imparted is the specific heat of the gas at constant pressure. In this case, the gas has done a certain amount of external work. It has pushed out the piston. The energy required to do this must come from the heat imparted, as there is no other source. The heat taken up by the gas at constant pressure is used partly to raise the temperature of the gas, and partly to provide the energy for the external work done. Therefore, to raise the temperature of the gas through 1°C. at constant pressure more heat must be applied than to bring about the same increase in temperature at constant volume, because part of the heat is, in the first instance, used in the performance of external work. The amount of the work done and heat used may be calculated.

Suppose we have a volume of gas v_1 and it expands to a volume v_2 at constant pressure p . Consider a small volume change dv . The work done will be $p dv$. The total work done over the whole volume change will be given by integrating $p dv$ between the limits v_1 and v_2 .

$$\int_{v_1}^{v_2} p dv = p(v_2 - v_1) = \text{pressure} \times \text{change in volume.}$$

$$= R(T_2 - T_1) = R \text{ (for } T_2 - T_1 = 1, \text{ and if we are dealing with 1 gm. mol. of the gas).}$$

$$= 2 \text{ gm.-cals.}$$

The molecular heat at constant pressure is therefore greater than that at constant volume by 2 gm.-cals. Hence,

$$C_p - C_v = R.$$

The symbols for specific heats at constant pressure and constant volume are C_p and C_v , and for their ratio, γ .

If the molecular heat at constant volume is $3 + x$ gm.-cals., that at constant pressure will be $5 + x$ gm.-cals., and the ratio of the specific heats will be $(5 + x)/(3 + x)$.

Thus

$$\gamma = C_p/C_v = (5 + x)/(3 + x).$$

If $x = 0$, $C_p/C_v = 5/3 = 1.667$.

This result may be expected only in the case of very simple molecules, and it is actually found for monatomic gases and vapours. Thus the



(a) Rotation. (b) Vibration.

ratio of the specific heats of the inert gases is 1.67. As the molecule becomes more complex, so the value of x increases. When we have a

diatomic molecule, there is a possibility of a rotational and a vibrational motion, as well as direct translation.

For most diatomic gases, it is found that $x = 2$, in which case, $C_p/C_v = 7/5 = 1.40$.

For triatomic gases, $x = 3$, and hence $C_p/C_v = 8/6 = 1.33$.

The following table will indicate how closely the ratio of the specific heats approximates to one or other of these numbers.

TABLE XXX.—RATIO OF SPECIFIC HEATS OF GASES AT 15° C.

Helium	1.666
Argon	1.67
Hydrogen	1.408
Oxygen	1.396
Nitrogen	1.405
Air	1.403
Carbon monoxide	1.404
Hydrogen chloride	1.400
Chlorine	1.355
Carbon dioxide	1.302
Nitrous oxide	1.300
Sulphur dioxide	1.285
Sulphuretted hydrogen	1.340
Steam (100° C.)	1.306
Ammonia	1.310
Acetylene	1.280
Methane	1.310
Ethylene	1.250

It must be borne in mind that the explanation of the value of x in the above work is not yet definitely established. However, the usual explanation is based upon the principle of equipartition of energy, which was deduced by Maxwell and Boltzmann. According to this principle, the energy imparted to a gas will be equally distributed between every degree of freedom. A degree of freedom is every possible mode of motion of a molecule.

Thus, in the case of a monatomic gas, the only type of motion possible is motion in a straight line, or motion that can be made up of small motions in a straight line. This motion can, however, be represented by three components mutually at right angles. The system therefore has three degrees of freedom. The kinetic energy of a molecule is $\frac{1}{2} mu^2$, and this can be resolved into the three components, connected by

$$\frac{1}{2} mu^2 = \frac{1}{2} mu_x^2 + \frac{1}{2} mu_y^2 + \frac{1}{2} mu_z^2.$$

Now, according to the theory of equipartition of energy,

$$\frac{1}{2} mu_x^2 = \frac{1}{2} mu_y^2 = \frac{1}{2} mu_z^2 = \frac{1}{2} \frac{R}{n} T,$$

because the total kinetic energy $\frac{1}{2} m n u^2 = \frac{3}{2} RT$.

Every degree of freedom of this motion is therefore associated with an amount of energy = $1/2 RT$ per gram-molecule. The total energy is $3/2 RT$, and the corresponding molecular heat capacity, $3/2 R$ cal. Gases of all kinds have translatory motion, and therefore they all have energy $3/2 RT$ corresponding to this motion, as well as any extra due to other types.

As has already been mentioned, a gas which has molecules made up of more than one atom may possess vibrational energy, which is both potential and kinetic. For a diatomic molecule this motion can only exist in one direction, *viz.*, along the axis of the molecule, and hence two degrees of freedom would be assigned to it, one for potential and one for kinetic energy. For a triatomic gas, such motion could, in general, take place along three directions—the sides of the triangle formed by joining up the centres of the atoms. In this case, then, there would be six vibrational degrees of freedom.

Consider now rotational motion. Molecules will rotate about their centre of gravity as a result of collisions with other molecules. Such motion is described in a plane, and is resolvable into two components, each of which would be assigned one degree of freedom. This assumes that the molecule is diatomic; or if polyatomic, the atoms must be arranged linearly. In the case of a triatomic gas where the atoms stand at the corners of a triangle, it might be expected that three degrees of freedom would result.

For a diatomic gas, then, we have three degrees of freedom for translation, two for rotation and two for vibration. If we assume the molecule to be rigid, the last two are lost, and so the energy is now $\frac{5}{2} RT$, or the

gas has a molecular heat capacity of 5 cal. per degree. This seems to be true for most diatomic gases, but it is possible, according to the theory, for a diatomic gas to possess seven degrees of freedom, and it would then have a molecular heat capacity of 7 cal. per degree.

124. The Determination of the Ratio of the Specific Heats of Gases.—Obviously this could be carried out by measuring the specific heat at constant pressure and at constant volume, and calculating their ratio, but, in addition, there are some indirect methods.

The direct determination of the specific heats of gases is a matter of some difficulty, since the volume of a given mass of gas is so large. Large volumes of gas have to be used if good results are to be obtained.

(a) *Direct Determination of C_p .*—This can be carried out by a modification of the method of mixture applied to the ordinary determination of the specific heat of a solid. The method, which was used by Regnault and others, consists in passing a known volume of gas heated to a definite temperature through a calorimeter containing cold water, and measuring the amount of heat liberated.

The continuous flow method of Callendar has also been used. The gas, heated to a definite temperature, is passed into a special form of continuous flow calorimeter, and is then heated electrically. The rise in temperature is measured by means of a platinum resistance thermometer. The method has been applied by Scheel and Heuse for low temperature determinations of C_p .

McCollum used a modification of Regnault's method to determine the specific heat of nitrogen tetroxide at constant pressure. The gas was passed through a spiral tube in a thermostat, the time taken for the gas to pass through the tube being sufficiently long to ensure that it attained the temperature of the bath. It then passed into a slightly warmer bath, the temperature of which was kept constant by an electric heater. The current flowing in the latter was measured. When the cool gas passed

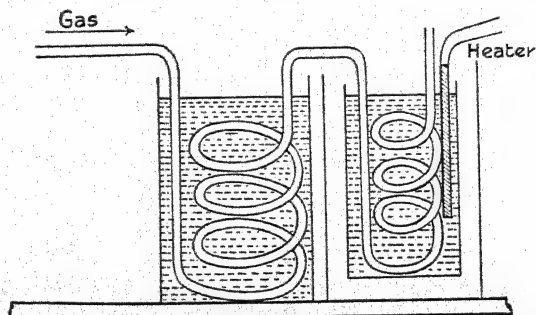


FIG. 64.—McCollum's Apparatus for determining the Specific Heat of Nitrogen Tetroxide at Constant Pressure.

into the warmer vessel, it tended, of course, to cool it. Additional current had to be passed through the heater to maintain the bath at constant temperature. The amount of this extra current was a measure of the heat absorbed by the gas. Let the mass of gas passing through the bath in 1 sec. be m gms. If the additional current flowing through the heater is I amperes, and its resistance is R ohms, then, in 1 sec. the amount of heat given out by the heater is $H = \frac{I^2 R}{4.184}$ calories. This is the amount of heat taken up by the mass of gas m , in raising its temperature from t° C. (the temperature of the thermostat) to t_1° C. (the temperature of the bath). If C_p is the specific heat of the gas at constant pressure,

$$mC_p(t_1 - t) = \frac{I^2 R}{4.184}$$

$$C_p = \frac{I^2 R}{4.184m(t_1 - t)}$$

(b) *Direct Determination of C_v .*—This is a somewhat more difficult operation. Joly used his steam calorimeter for this purpose (Fig. 65). This instrument consists of two thin copper spheres supported from the ends of a balance beam, and surrounded by a chamber which can be filled with steam. The two spheres should balance each other, and when steam is admitted into the chamber it will condense on the two spheres in equal amount, and hence they will still weigh the same. The spheres are first evacuated, and then one of them is filled with the gas to be investigated, under pressure. The steam is admitted, and it is now found that a different quantity of steam condenses on the sphere containing the gas from that condensing on the evacuated one. The difference is found by adding weights. The difference in the amount of steam condensed is due to the different heat capacities of the globes, and hence it is possible to obtain the specific heat of the gas.

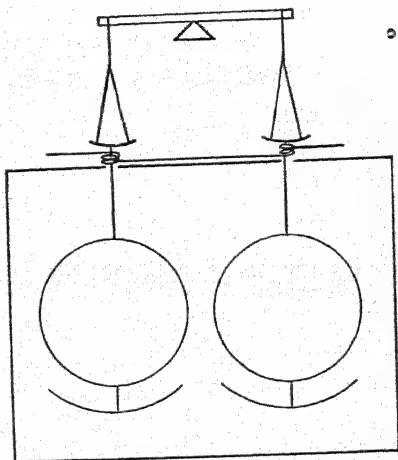


FIG. 65.—The Joly Steam Calorimeter.

The method has been modified by Eucken for work at low temperatures, and its accuracy has been considerably improved.

The explosion method, originated by Bunsen, and more recently modified by Pier, is rather interesting, and is capable of yielding fairly accurate results. The principle of the method is as follows: A gas that will explode with oxygen is admitted with the latter, and mixed with various indifferent gases, into a closed vessel. The mixture is exploded, and the maximum pressure reached is measured. From this the temperature to which the mixture has been heated can be calculated. Knowing the heat of the reaction (Chapter V.), and the heat capacity of the vessel, the heat capacity of the gas can be obtained. Pier used a special form of manometer, involving the use of a very thin steel plate, with a high period of vibration. The plate was deformed by the pressure increase due to the explosion, and the deformation was measured photographically, and compared with that produced by known pressures.

(c) *Indirect Methods of Determining C_p/C_v .*—(1) *The Method of Clément and Desormes* (1819).—To understand this method, it is necessary to be acquainted with the definition of an adiabatic change. An adiabatic change is one in which no heat is allowed to escape from, or be added to, the system during the change. The temperature in an adiabatic

change must, then, alter. It is here that it differs from an isothermal change in which there is no alteration in temperature.

In the Clément and Desormes' method, a large vessel is filled with the gas under observation to a pressure a little above atmospheric. This pressure is measured by means of a manometer attached to the vessel. The vessel is then opened for a very short while, during which the gas inside attains atmospheric pressure, and, in so doing, expands and cools a little. When the vessel is closed, the gas begins to attain room temperature again, and so its pressure again increases. The increase is measured.

In considering the theory of this experiment we may derive first the equation connecting the pressure and volume of a gas which undergoes adiabatic expansion. Consider one gram-molecule of a gas, and allow it to expand adiabatically from a volume V to $V + dV$, under constant pressure P . The work done is PdV . Suppose the temperature falls by dT . The amount of energy corresponding to the external work done is, therefore, $-C_v dT$, where C_v is the molecular heat at constant volume.

Hence
$$PdV = -C_v dT.$$

But
$$PV = RT,$$

$$R \cdot \frac{dV}{V} = -C_v \cdot \frac{dT}{T}.$$

Considering a volume change from V_1 to V_2 , the temperature falls from T_1 to T_2 . Hence

$$\int_{V_1}^{V_2} R \cdot \frac{dV}{V} = - \int_{T_1}^{T_2} C_v \frac{dT}{T}.$$

$$R \log_e \frac{V_1}{V_2} = C_v \log_e \frac{T_2}{T_1}.$$

But
$$C_p - C_v = R$$

(§ 123)

$$\therefore (C_p - C_v) \log_e \frac{V_1}{V_2} = C_v \log_e \frac{T_2}{T_1},$$

or
$$\log_e \frac{T_2}{T_1} = (\gamma - 1) \log_e \frac{V_1}{V_2},$$

or
$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1} \right)^{\gamma-1} \quad \left(\text{— incorrect} \right)$$

Since
$$P_1 V_1 = RT_1 \text{ and } P_2 V_2 = RT_2.$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma = \text{constant.}$$

and
$$P_1^{1-\gamma} T_1^\gamma = P_2^{1-\gamma} T_2^\gamma = \text{constant.}$$

Generally, the equations may be written

$$PV^\gamma = \text{constant.}$$

$$P^{1-\gamma} T^\gamma = \text{constant.}$$

$$TV^{\gamma-1} = \text{constant.}$$

This may now be applied to the conditions obtaining in the Clément and Desormes' experiment. Suppose the original pressure of the gas is P_1 , and atmospheric pressure is P . Let the final pressure be P_2 . Let T be the initial temperature, and t the decrease in temperature. Then, whilst the temperature of the gas rises from $T - t$ to T , its pressure increases from P to P_2 . Hence

$$\frac{P}{P_2} = \frac{T - t}{T}.$$

From the adiabatic equation given above,

$$P_1^{1-\gamma} T^\gamma = P_2^{1-\gamma} (T - t)^\gamma$$

$$\therefore \left(\frac{P_1}{P_2}\right)^{1-\gamma} = \left(\frac{T - t}{T}\right)^\gamma = \left(\frac{P}{P_2}\right)^\gamma$$

Taking logarithms of both sides of the equation,

$$(1 - \gamma) \log_e \left(\frac{P_1}{P_2}\right) = \gamma \log_e \left(\frac{P}{P_2}\right),$$

$$\therefore \gamma \left(\log_e \frac{P}{P_2} + \log_e \frac{P_1}{P} \right) = \log_e \frac{P_1}{P_2},$$

$$\therefore \gamma = \frac{\log_e \frac{P_1}{P_2}}{\log_e \frac{P}{P_2} + \log_e \frac{P_1}{P}} = \frac{\log_e P_1 - \log_e P_2}{\log_e P_1 - \log_e P}.$$

Hence γ can be determined by observations of the pressures P_1 , P_2 and P . No determination of temperature is necessary.

Lummer and Pringsheim (1898) improved the accuracy of this method by employing a very large vessel (90 litres capacity), and allowing the excess pressure to blow off through a large orifice. This made certain that the gas had actually reached atmospheric pressure. The temperature of the gas was determined immediately by means of a platinum resistance thermometer placed at the centre of the flask. Since the process is adiabatic, the formula to use is:—

$$\frac{T_1}{T_2} = \left(\frac{P_1}{P_2}\right)^{\frac{\gamma-1}{\gamma}}$$

where T_1 , P_1 are initial temperature and pressure, and T_2 , P_2 are the corresponding final conditions.

(2) *By Determining the Velocity of Sound.*—It was at first thought that the velocity, v , of sound in a gas was connected with its elasticity under isothermal compression, E , and its density, d , by the expression

$$v = \sqrt{\frac{E}{d}}.$$

Later it was found that the elasticity to be used was not that under

isothermal compression, but that under adiabatic compression, E_a ; for when a sound wave passes through a gas there is no time for the heat to

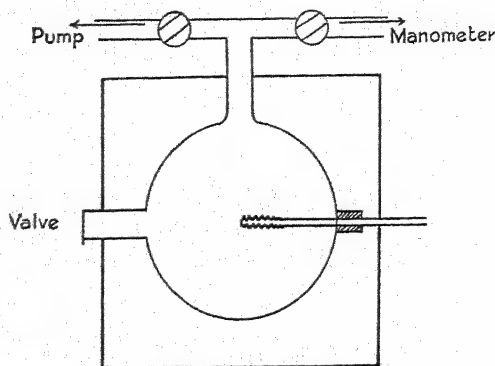


FIG. 66.—Lummer and Pringsheim's Modification of Clément and Desormes' Apparatus (diagrammatic).

be dissipated before the next pulse follows, so that the whole process is adiabatic. The velocity of sound in a gas is therefore given by

$$v = \sqrt{\frac{E_a}{d}}.$$

Now, E_a is related to E by the expression

$$\frac{E_a}{E} = \gamma = \frac{C_p}{C_v},$$

and E is identical with the pressure of the gas, p , so we have

$$E_a = p\gamma \text{ and } v = \sqrt{\frac{\gamma p}{d}}.$$

If now we have two gases of density d_1 and d_2 under the same pressure, the velocity of sound in the gases being v_1 and v_2 , respectively, and the ratio of the specific heats for the two gases γ_1 and γ_2 , we have

$$v_1 = \sqrt{\frac{\gamma_1 p}{d_1}} \quad v_2 = \sqrt{\frac{\gamma_2 p}{d_2}}$$

$$\therefore \frac{v_1^2}{v_2^2} = \frac{\gamma_1 d_2}{\gamma_2 d_1}.$$

Now, the velocity of a wave motion is connected with the wavelength λ , and frequency n , by the expression $v = n\lambda$.

If symbols with the suffixes 1 and 2 refer to the two gases, for a note of the same frequency, n ,

$$v_1 = n\lambda_1 \quad v_2 = n\lambda_2$$

$$\therefore \frac{v_1}{v_2} = \frac{n\lambda_1}{n\lambda_2} = \frac{\lambda_1}{\lambda_2} \quad \therefore \frac{\lambda_1^2}{\lambda_2^2} = \frac{\gamma_1 d_2}{\gamma_2 d_1}.$$

Hence,

$$\frac{\gamma_1}{\gamma_2} = \frac{\lambda_1^2 d_1}{\lambda_2^2 d_2} \quad (1)$$

Two practical methods are possible. Either the actual velocity of sound in a gas may be found, or the wavelength of the note of a given

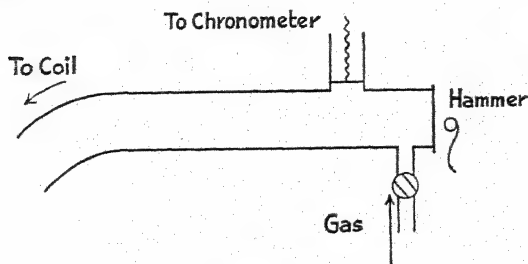


FIG. 67.—Dixon's Apparatus.

frequency may be determined. Until comparatively recently it has not been possible to carry out the first experiment because with the older methods such large quantities of gas were required. However, in 1921, Dixon determined the velocity of sound in certain gases directly, and in some cases over a considerable range of temperature. He first showed that the velocity of sound was the same in coiled tubes as in straight ones. He then sent sound waves through gases in coiled tubes, about 15 metres in length and 25 mm. in diameter. The sound wave was started by a hammer worked like an electric bell hammer, striking a steel diaphragm at the end of the tube. When the wave passed the platinum disc, a mark was made by a self-recording chronometric apparatus, and a similar piece of apparatus marked its arrival at the other end. In this way the time taken for the wave to travel the length of the tube was found. After correcting for the fact that the velocity of sound in tubes is not quite the same as that in the open, the velocity was calculated.

The value of γ could then be found from the equation

$$v = \sqrt{\frac{\gamma p}{d}},$$

but Dixon used, instead of the density d of the gas, the expression for the density from the molecular weight of the gas given by Daniel Berthelot (§ 127), giving as the final relationship

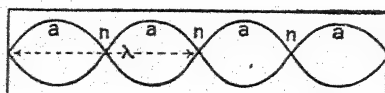
$$\gamma = \frac{v^2 M}{RT} \left[1 + \frac{9p}{128p_c} \cdot \frac{T}{T_c} \left(1 - 6 \frac{T^2}{T_c^2} \right) \right],$$

where M is the molecular weight of the gas, R the gas constant, T the

absolute temperature of measurement, T_c the critical temperature, and p_c the critical pressure.

The following results were obtained:—

	γ
Nitrogen	1.408
Carbon dioxide	1.296
Methane	1.301



n = nodes; a = antinodes; $na = \lambda/2$.

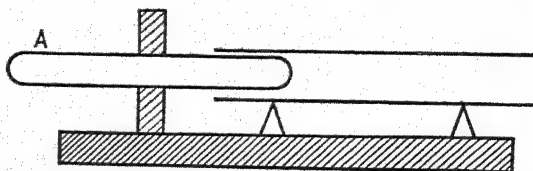


FIG. 68.—Behn and Geiger's modification of Kundt's method.

The second method mentioned is rather more convenient. In this the wavelengths of notes of the same frequency passed through two gases are compared. The apparatus is called Kundt's tube, although the modification described below has been devised by Behn and Geiger. The gas under test is placed in the dried sealed tube A, together with some lycopodium powder, or silica dust. The tube is clamped at its middle, and small discs of lead can be fixed to either end so that the tube may be made to vibrate. One end of the tube enters a wider, open tube, containing air and some lycopodium or silica dust. The sealed tube is stroked with a wet cloth, which sets it into vibration, and the air in the wider tube is also set into vibration by resonance. The powder in the tubes becomes heaped up at the places of least motion, i.e., at the nodes. The distance between two heaps will therefore be half a wavelength (Fig. 68). By measuring the distances, and multiplying by two, the wavelength of sounds of the same frequency in the gas and in air can be obtained.

The ratio of γ_1 to γ_2 for the two gases can be obtained by using formula (1) above, the density of the gases being known. If γ is known for one of them, the value for the other can readily be calculated. It should be noted that this is essentially a comparative method. This method was used by Ramsay and others in finding the ratio of the specific heats of the inert gases, although a slightly different apparatus was used. It is a little difficult to work with helium as, owing to its lightness, it does not give good dust heaps.

125. The Determination and Calculation of some Molecular Constants.

—(a) *The Mean Free Path.*—The mean free path has already been defined as the mean distance through which a molecule can move without coming into collision with another. Of course, the actual distance through which a molecule moves before collision varies enormously from time to time. Sometimes it may travel a long distance before meeting another molecule; at other times only a fraction of the mean free path is traversed. The viscosity of a gas will obviously be directly connected with the mean free path. The *coefficient of viscosity*, η , is defined as *the force per unit area exerted between two parallel layers at unit distance apart, when the velocity of streaming differs by unity in the two layers.*

From the kinetic theory it may be shown that

$$\eta = \frac{1}{3} d \lambda u$$

where λ is the mean free path, d is the density, and u the root-mean-square velocity.

If we substitute the value of u obtained in § 121,

$$u = \sqrt{\frac{3p}{d}}$$

in this equation, the expression

$$\lambda = \eta \sqrt{\frac{3}{pd}}$$

is obtained.

As would be expected, the mean free path is greater the lower the pressure. The value of the mean free path can therefore be obtained from observations of viscosity.

The collision frequency, which is given by $\frac{u}{\lambda}$, can also be obtained quite easily.

It will be seen from Table XXXI. that the mean free path of oxygen at N.T.P. is of the order of 10^{-5} cm. It is twice this in hydrogen. For comparison, the average wavelength of light in the visible spectrum is 5×10^{-5} cm. At low pressures the mean free path may amount to several centimetres.

In 1 second, a molecule describes as many free paths as it makes collisions, and hence the sum of the free paths is equal to the mean speed. Taking the case of hydrogen, the root-mean-square velocity, η , is 183,800 cm. per second, and the mean free path is 17.8×10^{-6} cm. Hence the number of collisions per second is

$$\frac{u}{\lambda} = \frac{183,800}{17.8 \times 10^{-6}} = 10,330 \times 10^6.$$

It need not be pointed out that this number is very large. It might be

noted, however, that even when the mean free path is increased to 1 cm., which could happen at very low pressures, the number of collisions per second is 183,800, i.e., nearly 200,000 per second.

TABLE XXXI.—MEAN FREE PATHS (AT N.T.P.)

Hydrogen	17.8×10^{-6} cm.
Oxygen	10.0×10^{-6} „
Nitrogen	9.5×10^{-6} „
Carbon dioxide	6.3×10^{-6} „
Carbon monoxide	9.3×10^{-6} „
Water vapour	7.2×10^{-6} „

(b) *Avogadro's Number*.—Avogadro's Law states that equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules. It is interesting to know how many molecules there are in a gram-molecule of a gas. This should be the same for all gases, and is called Avogadro's number, N . Occasionally, we meet with the number of molecules contained in 1 c.c. of gas at N.T.P. This is called Loschmidt's number, and is denoted by n . It is obvious that

$$N = 22,414n,$$

since one gram-molecule of a gas occupies a volume of 22,414 c.c.

Avogadro's number can be determined by a variety of experimental methods, which give surprisingly concordant results. A few of these methods are described.

(1) *The Method of Rutherford and Geiger*.—The element radium is continually shooting out helium nuclei, called α -particles (Chapter II., § 21). They move very rapidly, in fact, about 100,000 times as fast as an ordinary gas molecule. They possess the property of causing zinc sulphide to glow when they fall upon it. If, then, the α -particles are

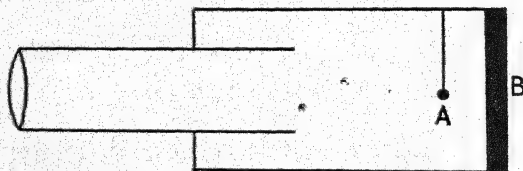


FIG. 69.—Spinthariscopes (diagrammatic).

not shot off too frequently it is possible to count them, since every time they impinge on a zinc sulphide screen they cause a flash. The apparatus for counting the α -particles is shown in Fig. 69 and is called a spinthariscopes. The radium preparation A, was hung in front of the zinc sulphide screen B, which was viewed through a lens. A separate

experiment was carried out to find out how much helium was formed from a larger, known amount of radium, in a given time. The volume of the gas and the number of atoms in it were known, because they had been directly counted as α -particles. Hence the number of atoms (of helium; molecules of any other gas) in 1 c.c. could be calculated, and from this Avogadro's number could be obtained. Allowance was made for the fact that only a fraction of the α -particles strike the screen. The results obtained for the experiments were:—

$$\begin{array}{lcl} \text{Number of molecules per c.c.} & = & 2.7 \times 10^{19} \\ \text{Avogadro's number} & = & 6.05 \times 10^{23} \end{array}$$

The method was improved in 1908, the apparatus depicted in Fig. 70 being used. A long glass tube, TT, 450 cm. long, and 2.5 cm. wide, called the firing tube, was exhausted, and a radium preparation on a lead plate was placed at A. Some α -rays shot along the tube, passed through the narrow tube B, and passed into the ionisation chamber C, through the window F. The gas in the ionisation chamber, which was at low pressure, became ionised every time an α -particle passed into it, and this rendered the gas conducting. A current then passed through the electrometer (which was connected to the wire w , and the outside of the chamber), every time the gas was ionised. It was thus possible to count the α -particles, and knowing the volume of helium produced in a given time, obtained by a separate experiment, Avogadro's number could be found. The value obtained was

$$N = 6.14 \times 10^{23}.$$

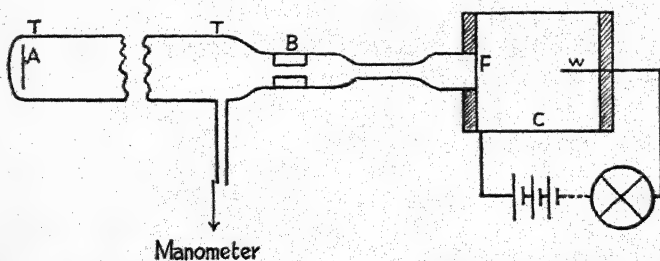


FIG 70.—Rutherford and Geiger's Apparatus (diagrammatic).

Allowance was made for the fact that only a fraction of the α -particles got into the ionisation chamber. It may be noted that in the spinthariscopes method the minutest quantity of radium is used, whereas the second method requires an appreciable quantity.

(2) *Perrin's Method*.—This is based on a study of the Brownian Movement (Chapter XI/II.). If very fine particles are suspended in a liquid and are examined under the ultramicroscope, it is found that they are moving about rapidly and with random motion. This motion is

called the Brownian Movement, because it was first observed by the botanist Brown, with pollen grains. The reason why the particles are moving about in all directions is because they are continually being bombarded by molecules of the medium in which they are placed. This bombardment will affect them differently from time to time, for at one instant they may be hit by many or rapidly moving molecules, and at other times by few or slowly moving molecules. Hence their motion is continually varying. Perrin supposed that a particle suspended in a liquid would behave just like a large molecule and would possess the same mean kinetic energy as a molecule of the liquid. He calculated the way in which gravity should cause an alteration in the numerical density of these particles in a column of fluid. Owing to their weight, there will be a larger number at the bottom than elsewhere, and this number will get smaller and smaller as we go up the column. Two effects have to be taken into account. The first is gravity, which causes a downward motion, and the second is a diffusion upwards. Perrin obtained the following expression:—

$$\frac{2}{3} w \log \frac{n_0}{n} = \phi (D - \delta) g h,$$

where w is the mean kinetic energy of the particle; n_0 and n the average number of particles per unit volume at levels which differ in height by h ; ϕ the volume of a particle; D and δ the densities of the particles and the liquid respectively. Perrin set out to determine w experimentally, making use of this expression, and it will be seen that in order to do so it is necessary to determine the volume of a particle, and the numbers present at given heights in the medium. The volume of the particle was found by counting the number in a given volume of suspension, which was then evaporated to dryness, and the weight of the remaining particles determined. The weight of one particle could thus be found, and knowing the density of the particle (which was assumed by Perrin to be the same in the particle as in the bulk condition, though it need not necessarily be), the volume could be calculated. The number of particles at different levels was obtained by focusing a microscope on a certain level and counting the number, and then turning the focusing screw so as to raise the objective through a given distance. This would now be focused on a new layer, at a distance from the previous one equal to the distance through which the microscope had been raised. The number of particles in the newly focused layer was then counted. w can thus be calculated.

We have already seen (§ 118) that the mean kinetic energy of a molecule is given by

$$w = 3pv/2n.$$

For a gram-molecule of a gas, which contains N molecules,

$$pv = RT.$$

Hence

$$w = 3RT/2N.$$

Knowing w , N can be found.

The value obtained by this method was

$$N = 6.90 \times 10^{23},$$

which is in very good agreement with the Rutherford and Geiger value.

(3) *The Millikan Oil-Drop Method.*—This method, which has already been described in connection with the determination of the charge of the electron, can be utilised to furnish a value for Avogadro's number by using the relationship that the number of electrons in one gram-molecule of ions is N , and if e is the charge on one, and F the Faraday, then $Ne = F$ (§ 26).

F is readily found by electrolysis experiments; e is found by Millikan's method, as previously described, to be 1.59×10^{-19} coulombs; hence $N = 6.062 \times 10^{23}$, if $F = 96,500$ coulombs. This is probably the most accurate method of determining N .

Quite a number of methods have been used to determine Avogadro's number, and all give concordant results, some of which are given in the table below. This fact alone shows that there can be no doubt about the existence of molecules.

TABLE XXXII.—VALUES OF N .

Classical kinetic theory	10×10^{23} (approx.)
Brownian movement (Perrin)	6.90×10^{23}
Radiant heat	6.19×10^{23}
Counting α -particles	6.14×10^{23}
Electronic charge (Millikan)	6.06×10^{23}
Brownian movement (Nordlund)	5.90×10^{23}

(c) *The Mass of the Molecule.*—Knowing Avogadro's number, we can calculate the mean mass of the molecules, if the gram-molecular weight of the gas is known. Thus, for oxygen, the gram-molecular weight is 32. Hence the mass of the oxygen molecule is

$$\frac{32}{6.06 \times 10^{23}} = 5.28 \times 10^{-23} \text{ gm.}$$

The mass of the hydrogen atom calculated in a similar way is 1.663×10^{-24} gms.

126. *Deviations from Boyle's Law.*—Boyle's experiments were

carried out within a comparatively small pressure range, and were not sufficiently accurate to show whether the law was strictly correct or not. At the beginning of the nineteenth century many people attempted to verify the law, but the best work was done by Regnault in 1847.

He improved the apparatus so as to reduce the experimental error, and also increased the pressure range up to 27 atmospheres. He found that the gases he used, hydrogen, nitrogen, air and carbon dioxide, did not obey the law perfectly. Hydrogen was found to be less compressible, and the other gases more compressible, than the law demands.

The work of Regnault was improved upon by Amagat, who carried out experiments first up to a pressure of 400 atmospheres, using a mercury manometer. For this purpose, the mercury tube was placed in the shaft of a coal mine. By using a hydraulic press, he was able in a later series of experiments to reach 3,000 atmospheres.

The results of these experiments showed that no gas strictly obeys Boyle's Law. Gases are therefore not perfect, a perfect gas being defined as one which obeys Boyle's Law. The nature of the deviations are best shown by plotting the product of pressure and volume against pressure. If a gas obeyed Boyle's Law this curve would be a straight line, the line AB in Fig. 71.

It will be noticed that the curve for hydrogen starts ascending at once, whilst for the others the curves all show a decrease in p_v at first.

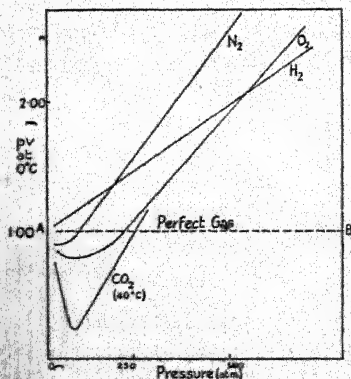


FIG. 71.—Graph of p_v against p for nitrogen, hydrogen, oxygen, and carbon dioxide, based on Amagat's results. The ordinates represent the relative deviation of p_v for the gas from the value for a perfect gas (1.00). In deducing p_v , v is taken as 1, when $p = 1$ atmosphere.

Ultimately, all gases behave like hydrogen, above, say, about 400 atmospheres. It has been shown that the inert gases give curves exactly like that of hydrogen. The gases which are most easily liquefied deviate the most from Boyle's Law.

Experiments on gases at low pressures have not yet shown definitely whether gases deviate from the law at extremely low pressures.

127. Modifications of Boyle's Law.—The fact that experiment reveals deviations on the part of most gases from Boyle's Law must be explicable on a theoretical basis. Boyle's Law has been derived in a previous section (§ 117) from the kinetic theory. It is possible that the assumptions upon which the kinetic theory is based are at fault.

It will be remembered that in deriving Boyle's Law certain assumptions were made about the size, shape and properties of molecules. In the derivation, it was tacitly assumed that the molecules had a negligible volume, and that there were no attractive forces between them. Both these assumptions are, of course, not true at ordinary temperatures and pressures. When the pressure of a gas is considerably reduced the volume occupied by the molecules may be negligible when compared with the space in which they move, but not under ordinary conditions.

In 1865, Hirn put forward an equation which took the first of these corrections into account. If the molecules do occupy some volume, then the space available for their motion must be reduced, and so, in the ordinary Boyle's Law equation, $pv = RT$, we must substitute for v , $(v - b)$, where b is a quantity dependent upon the volume occupied by the molecules. It is not a difficult mathematical exercise to show that it should correspond to four times the volume of the molecules.

A correction was also attempted for the second error, the attractive force exerted by the molecules on each other. That such an attractive force exists is shown by the Joule-Thomson effect (§ 165). For a molecule in the centre of the gas the attraction of other molecules will, on the average, be spread over a sphere uniformly, and so need not be taken into account for our purpose. Molecules near the edges will, however, experience an attractive force which tends to drag them inwards, and so the velocity with which they strike the walls, and the corresponding pressure, will be lower. Thus the observed pressure is less than that which would be exerted if there were no attractive force. Hirn therefore proposed to add a pressure, P_i to p , in order to increase the pressure to the value it would have if there were no attraction. P_i was called the intrinsic pressure, or the internal pressure of the gas.

Hirn's modification of Boyle's Law therefore reads:—

$$(p + P_i)(v - b) = RT.$$

Van der Waals (1873) carried the matter further. He added a factor $\frac{a}{v^2}$ to the pressure to account for the attraction of the molecules for each other. The correction will depend upon (i) the number of molecules in the surface layer, and (ii) the number of molecules in the interior. Both these numbers are proportional to the density i.e. (for a given mass of gas), inversely proportional to the volume. Hence the form of the correction. Van der Waals' equation is therefore

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT. \quad \checkmark$$

The equation of Van der Waals correctly explains the general behaviour of gases, and, incidentally, also of liquids, throughout the whole range of temperatures and pressures, but quantitative agreement

with experimental data is still not quite exact. Hence, many equations, most of them empirical, have been put forward to cover the experimental facts. It would be useless to consider all of them, because well over a hundred modifications of van der Waals' equation have been proposed. The most important of them are the equations of Dieterici, of Clausius, and of Berthelot. Dieterici made allowance for the density gradient at the boundary of the gas as the internal pressure diminishes to zero. The equation is

$$p(v - b) = RTe^{-\frac{a}{RT}},$$

where e is the base of natural logarithms.

Over small ranges of pressure, Dieterici's equation agrees with that of van der Waals, but at high pressures the differences become quite appreciable, and, in general, Dieterici's equation explains the experimental facts better.

It was at first thought that the a factor in van der Waals' equation was independent of temperature. Amagat's work on carbon dioxide showed that this was not so, and Clausius modified van der Waals' equation accordingly, by putting the term $a/[T(v + c)^2]$ for a/v^2 . The Clausius equation is therefore

$$\left(p + \frac{a}{T(v + c)^2}\right)(v - b) = RT.$$

It explains the relationship between pressure, temperature and volume reasonably well for some gases, but its success is not general.

The equation of Daniel Berthelot depends upon the critical constants of the gas concerned. As explained in the next chapter, the van der Waals' constants a and b have been found to bear a relationship to the critical constants of a gas (§ 163). Berthelot derived an empirical relationship between the constants a and b , and the critical constants, and substituted their values in the van der Waals' equation, obtaining the equation

$$pv = NRT \left[1 + \frac{9}{128} \frac{p}{p_c} \cdot \frac{T_c}{T} \left(1 - 6 \frac{T_c^2}{T^2} \right) \right]$$

where p_c and T_c are the critical pressure and temperature, respectively.

Berthelot's equation gives very accurate agreement between observed and calculated values, but it must be remembered that it applies only to a pure gas, i.e., to a gas consisting of a single species of molecules only. The equation gives good results in the neighbourhood of the critical point, when others fail. It can be applied to saturated vapours.

128. Deviations from the other Gas Laws.—(a) *Avogadro's Hypothesis.*—Just as there are deviations from Boyle's Law, so the other gas laws are found to be not strictly accurate. It will be remembered that Avogadro's Hypothesis was derived on the basis of the kinetic theory

from the result obtained for Boyle's Law (§ 119). If the latter is wrong, being based on wrong assumptions, it follows that Avogadro's Hypothesis must be incorrect also. This is indeed the case. Equal volumes of gases under the same conditions of temperature and pressure do not contain the same number of molecules, and the usual statement of Avogadro's Hypothesis is probably only valid at very low pressures where the gases may behave as perfect gases, and where Boyle's Law itself may be obeyed.

It follows from this that the usual method of deriving the molecular weight of a gas from its density, merely by multiplying the latter by two (§ 11), does not give strictly accurate results, since this procedure implies the truth of Avogadro's Hypothesis. If, however, the gas volume were to be measured at low pressures, the hypothesis would become more exact, and at zero pressure it would probably be quite exact. Of course, this is an impossible condition for measurement, but the density at zero pressure can be approximated to.

A clearer idea of the quantities to be measured may be gained by considering the subject in greater detail. Suppose a mass W gms. of gas occupies a volume v litres at 0° C. under a pressure of p atmospheres. The quotient W/pv is called the density per unit pressure. If the gas obeys Boyle's Law, pv is constant, and obviously the above quotient remains constant over the whole pressure range, but if the gas does not obey Boyle's Law, there is a continuous variation of W/pv as the pressure varies. If the limiting value of pv is taken as p approaches zero, and the value of pv is then p_0v_0 , W/p_0v_0 is called the limiting density of the gas. This is the value to be used in determining molecular weights of gases.

If p_1v_1 is the value of pv when the pressure is one atmosphere, then obviously W/p_1v_1 is the normal density of the gas as commonly measured. Hence

$$\text{limiting density} = \text{normal density} \times (p_1v_1/p_0v_0).$$

It is thus a matter of some importance to determine the value of p_1v_1/p_0v_0 , and this can be done by two distinct methods. The first is the extrapolation method. A number of determinations of pv are made for different pressures, and these are plotted and the curve extrapolated to zero pressure. This method is the one usually followed and is exemplified by the determinations of the atomic weights of nitrogen and phosphorus from the densities of their gaseous hydrides.

The second method depends on the assumption that the relative deviation from Boyle's Law is proportional to the pressure, and is obviously applicable only to those gases which do not greatly deviate from Boyle's Law. The relative deviation is

$$\frac{p_0v_0 - pv}{pv}$$

Hence, with the above assumption,

$$\frac{p_0 v_0 - p v}{p v} = \alpha p.$$

α is known as the compressibility coefficient, and its value is obtained by taking two readings of $p v$ between 0 and 1 atmosphere. In this case

$$p_0 v_0 = p_1 v_1 (1 + \alpha) \quad (1)$$

since $p_1 = 1$.

Thus, the limiting density = normal density/(1 + α).

Avogadro's Hypothesis can then be applied to the limiting density found by these methods.

It is clear that the expression (1) implies a linear relationship between $p_0 v_0$ and $p_1 v_1$. Whilst this is true in the majority of cases, there are some substances for which it is not true. For these a curved extrapolation must be used, and it was suggested by Guye that the result should be expressed in the form $p_0 v_0 = p_1 v_1 (1 + \lambda)$. It has been pointed out by Cawood and Patterson that λ has no physical significance like α , although it is frequently wrongly called the compressibility coefficient. It may perhaps be called the "effective compressibility coefficient".

As examples of the use of these equations the figures obtained by Moles and Sancho for the density of ammonia, may be quoted.

Pressure.	Density per Unit Pressure.
Atmos.	Gms. per litre.
1	0.77169
0.667	0.76773
0.5	0.76585
0.33	0.76383

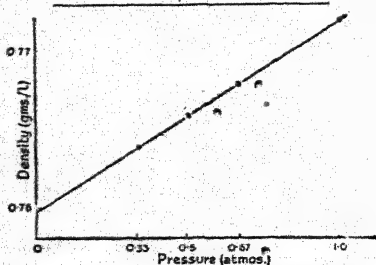


FIG. 72.—Graph of Pressure against Density per Unit Pressure for Ammonia.

These values are plotted in Fig. 72, and the curve continued to cut the density axis. The limiting density is found to be 0.759877 gm. per litre.

The limiting density of oxygen determined in the same apparatus is 1.42761 gm. per litre, so the density of ammonia referred to oxygen as 16 is

$$\frac{0.759877}{1.42761} \times 16 = 8.51636.$$

The molecular weight of ammonia is therefore 17.0327. Assuming the atomic weight of hydrogen to be 1.0080, this gives for the atomic weight of nitrogen 14.0088. The accepted value is 14.008.

Batuecas has determined the density of nitrous oxide. The following results were obtained:—

Pressure.	Density per Unit Pressure.
Atmos.	Gms./litre.
1	1.9804
0.667	1.9746
0.5	1.9722
0.25	1.9694

and

Pressure, p .	pv .
Atmos.	
1	1.00000
0.667	1.00294
0.5	1.00416
0.33	1.00559

By extrapolation of the curve between p and pv , the value for $p_0 v_0$ was obtained, and $(1 + \lambda)$ came out to be 1.0085. The limiting density is therefore $\frac{1.9804}{1.0085} = 1.9623$ gms. per litre.

The accepted figure for the volume occupied by one gram-molecule of a gas at N.T.P. is 22.414 litres.

Hence the molecular weight of nitrous oxide is $22.414 \times 1.9623 = 44.014$, and the atomic weight of nitrogen is $\frac{1}{2}(44.014 - 16) = \frac{1}{2}(28.014) = 14.007$.

The matter can be viewed in a somewhat different way. If Boyle's Law is true,

$$pv = RT,$$

where v is the volume occupied by one gram-molecule, R has its usual value (in litre-atmospheres) $p = 1$, and $T = 273^\circ$ Abs.

If M is the molecular weight, and D the density in grams per litre,

$$M/v = D$$

But,

$$v = RT/p.$$

Hence

$$M = DRT/p.$$

This equation enables the molecular weight to be calculated if the density D is known at some temperature T , and pressure p , and holds, if Boyle's Law is true. This, however, is not the case. If we use Berthelot's equation (§ 127), it is obvious that

$$M = \frac{DRT}{p} \left(1 + \left\{ \frac{9T_c(T^2 - 6T_c^2)}{128p_cT^3} \right\} p \right),$$

which may be written

$$M = \frac{DRT}{p} (1 + Ap),$$

where A stands for the expression in brackets. From this relationship it is possible to calculate the molecular weight of a gas very accurately, if the critical data are known.

As an example we can calculate the molecular weight of nitrogen from the following data:—

Density at N.T.P. = 1.2507 gms. per litre.

Critical temperature = 125.96° Abs. $R = 0.08204$ litre-atmos.

Critical pressure = 33.49 atmos.

Substituting in the equation

$$M = \frac{DRT}{p} \left(1 + \left\{ \frac{9T_c(T^2 - 6T_c^2)}{128p_cT^3} \right\} p \right)$$

we have

$$\begin{aligned} M &= 1.2507 \times 0.08204 \times 273 \left(1 + \frac{9 \times 125.96 (273^2 - 6(125.96)^2)}{128 \times 33.49 \times 273^3} \right) \\ &= 1.2507 \times 0.08204 \times 273 (1 - 0.0002689) \\ &= 1.2507 \times 0.08204 \times 273 \times 0.9997311 \\ &= 28.01. \end{aligned}$$

Thus the molecular weight is 28.01.

If the density of a gas is known under two conditions of pressure and temperature, it is possible to calculate its true molecular weight, using the Berthelot equation, without knowing the critical temperature and pressure.

Thus, the density of neon at 0° C. and 0.5 atmos. is 0.44986 gm. per litre, whilst that at N.T.P. is 0.9002 gm. per litre.

In both cases

$$\begin{aligned} A &= \frac{9T_c(T^2 - 6T_c^2)}{128p_cT^3}, \\ &= \frac{9T_cT^2}{128p_cT^3} - \frac{54T_c^3}{128p_cT^3}, \end{aligned}$$

$$= \frac{k}{T} - \frac{k'}{T^3},$$

$$= \frac{k}{273} - \frac{k'}{(273)^3}.$$

Since the temperatures are the same A will be the same, and the above process is not necessary; but where the temperatures are different it would have to be applied. Using the equation

$$M = \frac{DRT}{p} (1 + Ap),$$

for the first conditions

$$M = \frac{0.44986 R \times 273}{0.5} (1 + A (0.5)).$$

For the second conditions

$$M = 0.9002 R \times 273 (1 + A) \quad (1)$$

$$\therefore 0.44986 \times 2 \times 273 R \left(1 + \frac{A}{2}\right) = 0.9002 R \times 273 (1 + A),$$

$$\text{or} \quad 0.44986 \left(1 + \frac{A}{2}\right) = 0.4501 (1 + A)$$

$$\therefore A = -0.001066.$$

It is simplest to get M from equation (1);

$$M = 0.9002 \times 0.08204 \times 273 \times 0.998934$$

$$= 20.14.$$

(b) *Gay-Lussac's Law of Volumes*.—It has been found by experiment that Gay-Lussac's Law is not quite true. For example, Burt and Edgar found that the combining volumes of hydrogen and oxygen to form water were 2.00288 to 1. Gray and Burt found that two volumes of hydrogen chloride gave 1.0079 volumes of hydrogen. Guye and Pintza found that one volume of nitrogen combined with 3.00172 of hydrogen to give ammonia. It is thus obvious that the law is not quite exact.

The deviations from the law exist because Avogadro's Law is not quite true, and this in turn depends upon the inaccuracy of Boyle's Law. At very low pressures, like Avogadro's Law, it would probably be true.

SUGGESTIONS FOR FURTHER READING

PARTINGTON, J. R. "An Advanced Treatise on Physical Chemistry." Volume I. (*Longmans*, 1949.)

JEANS, J. H. "The Kinetic Theory of Gases." (*Cambridge University Press*, 1952.)

PERRIN, J. "Atoms" (trans. D. L. HAMMICK). (*Constable*, 1923.)

A good review of work on Limiting Densities, by R. Whytlaw-Gray, will be found in "Quarterly Reviews", vol. 4, 1950, pp. 153-171, published by the Chemical Society

CHAPTER VIII

THE SOLID STATE

129. Characteristics of Solids.—When a gas is cooled or submitted to pressure it becomes liquid, and in this state the molecules are much more closely packed than they are in the gaseous state. They have not the freedom of motion that they enjoy in the form of a gas, and thus a liquid is much more difficult to compress than a gas. If a liquid is cooled it becomes crystalline, possessing even smaller compressibility than before. Indeed, now the molecules have very little capacity for motion, arranging themselves in a definite order which gives rise to the crystalline structure of the solid.

It was thought until recently that all solids were crystalline, and that there were no truly amorphous solids. Many solids which appear to be amorphous are, in fact, supercooled liquids. Glass is one of these. Some workers regard this as a fourth state of matter, called the vitreous state. However, Riley has obtained truly amorphous carbon, and it would therefore seem that the solid state must include both crystalline and amorphous substances.

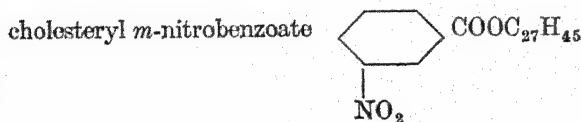
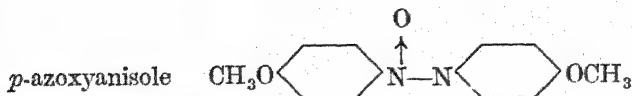
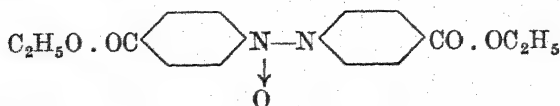
Every crystalline substance is made up of an assembly of smaller units all having the same geometrical form. Although a crystal is quite homogeneous, it possesses different properties in different directions, and is therefore said to be *anisotropic*.¹ Thus, crystals conduct heat and electricity better in one direction than in another. The index of refraction may vary in different directions in a crystal.

Much information is now available concerning the arrangements of molecules and atoms inside the crystal. Such arrangements determine crystalline form, and are described later (§ 134).

130. Liquid Crystals.—Crystals are usually regarded as possessing a certain rigidity, by reason of which they are called solids. Yet, there are a number of substances in which the weakness of the crystal forces results in lack of rigidity. These are called "*liquid crystals*". They will actually flow, and will rise up a capillary tube, showing that the surface forces which result in surface tension are strong enough to overcome the weak crystal forces. These substances are not intermediate between the two states—liquid and crystalline. It is merely a question of the weakness of the crystal forces, which are not sufficiently powerful to support a definite geometrical form. In order to avoid the confusion which might arise from the use of the name "*liquid crystals*", the term "*mesomorphic state*" has been used.

¹ Cubic crystals (§133) are fully symmetrical, and are therefore isotropic.

Liquid crystals possess a definite melting point at which they become true liquids, and are doubly refracting. Examples of substances which can form liquid crystals, of which some three hundred are known, are:—ethyl *p*-azoxybenzoate



When the solid substance giving liquid crystals is heated it appears to melt at a given temperature, forming a cloudy liquid which shows anisotropic properties, as mentioned above. The cloudy liquid represents the mesomorphic state. Some substances have been examined by means of X-ray analysis (§ 134) in the liquid-crystal state, and faint indications of crystalline structure have been obtained.

The effect of a magnetic field on liquid-crystals is interesting. Substances in the mesomorphic state are turbid, but when a magnetic field is applied they become clear, in the direction of the lines of force. The explanation of this, as well as of the double-refraction shown by liquid-crystals, probably lies in the arrangement of the molecules. Vorländer has pointed out that all substances which are capable of existing in the mesomorphic state have long or flat molecules. This would be expected from an examination of the formulæ given above. It may be supposed that when one of these substances is melted, the cohesion between the molecules, which previously held them in the crystal arrangement, does not break down uniformly in all directions. There may be a lateral cohesion which still exists, which will tend to hold the molecules together in bundles. This makes the liquid anisotropic. The properties may be expected to be different in different directions, for rudimentary crystals still exist. When the magnetic field is applied, all these bundles orient themselves in the same direction, along the lines of force, and the liquid clears in this direction.

The viscosity of liquid crystals is small, whereas that of liquids with

heavy molecules is usually large. It is evident, then, that the peculiar properties of the mesomorphic state are not due to mere polymerisation.

When a solid which can exist in the mesomorphic state is heated it changes into that state at a definite temperature, called the transition point. Then, on further heating, the mesomorphic state disappears, and the true liquid state takes its place. The temperature at which this occurs is the melting point. Thus, for *p*-azoxyanisole, the transition point is 118.3°C ., and the melting point 135.9°C .

• 131. **The Process of Crystallisation.**—From the point of view of theory, it is a fairly simple matter to draw a picture of what happens when crystallisation takes place. In a liquid the molecules are moving with random motion. They possess all sorts of velocities—some very high (molecules possessing these escape from the surface as vapour), and others below the average. Those molecules with low velocities obviously have a kinetic energy below the average, and when they happen to come together more or less in a certain arrangement corresponding to the crystalline form of the substance, the forces which hold the crystal together are strong enough to keep the molecules together. They may remain together for some time, or they may meet a molecule moving with high velocity, and therefore possessing high kinetic energy. This molecule, on collision, causes them to separate. Consider now a liquid which is cooling. Here the kinetic energy of the molecules is getting less and less, for heat is being given out, and hence the conditions for long life of the crystal nucleus are more advantageous. Finally, when the liquid cools sufficiently, the crystal forces are strong enough to overcome the bombardment by molecules which have too great a velocity to be added to the crystal nucleus, and the liquid crystallises. The crystal nucleus has the power of attracting other molecules to it by virtue of the crystal forces, and it forms a trap for all molecules which do not possess sufficient energy to escape. So the crystal grows.

When a crystal is heated, the reverse change may be supposed to take place. The molecules are gaining energy, which gives them a greater vibration in the crystal arrangement, which is called the crystal lattice. Finally they gain sufficient energy to break down the crystal lattice, overcoming the crystal forces, and the crystal melts.

At all temperatures the constituent particles of a crystal (atoms, molecules, or ions) are in vibration. This vibration persists even at absolute zero; at this temperature the particles possess an energy known as zeropoint energy. They are not moving very far, but very fast. According to a calculation by Mrs. Lonsdale their frequency of vibration is about 10^{13} per sec., so that in 24 hrs. the sodium ions in a sodium chloride crystal each travel about 50,000 miles, although they are never more than 0.23 \AA units from their lattice point.

It must be understood that the molecules are always oscillating in fixed mean positions in the crystal lattice, but they have not the power

of translational motion. Sometimes, however, a molecule may oscillate so violently that it breaks away from the crystal and goes directly into the vapour state. This explains why a crystal has a vapour pressure.

It is clear that heat will be required to give the molecules sufficient amplitude of oscillation to break down the lattice. This is the heat that is commonly referred to as latent heat of fusion. It is taken in when a substance melts, and is given out when it solidifies from the liquid state.

The above is merely a theoretical picture of the crystallisation process. In practice the way in which crystals are formed and the significance of crystal forces are still little understood. Tammann suggested that there are two definite processes involved in crystallisation. They are first, the formation of the crystal nuclei, and second, their growth. Each process must be studied separately.

It has been found possible to count the number of crystallisation nuclei formed when a liquid is cooled and supercooled under various conditions. It has been shown that the number of nuclei increases with decrease of temperature as this is reduced below the freezing point, passes through a maximum, and then decreases. If the number of nuclei formed is plotted against the temperature a curve of the type shown in Fig. 73 is obtained. It is clear that this is a typical probability curve, so that the formation of nuclei is governed by probability.

It has also been found that the rate of formation of nuclei is dependent to a great extent upon the presence of dust particles, and upon mechanical agitation. Indeed without the presence of these, supercooling usually occurs.

Turning to the other side of the matter—the rate of growth of the crystal once the nucleus has made its appearance—it has been found, as a result of the work of Gernez and of Tammann and his pupils, that this increases at first with decrease of temperature, then remains constant over a considerable temperature range, and finally falls rapidly. If the conditions are such that there is slow formation of nuclei and rapid growth, a few large crystals will result. If, on the other hand, the conditions are favourable to the growth of a large number of nuclei, but slow growth of crystals, there will be a large number of small crystals.

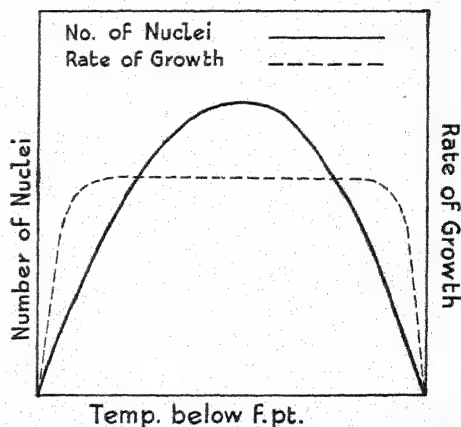


Fig. 73.

The study of the growth of crystals, particularly as regards their form during this period, shows that they undergo continual change. A perfect crystal is best made by very slow growth, during which a number of facets, in the usual course of events never seen, appear and disappear.

Spangenburg and Neuhaus (1928) turned a sphere from a single crystal of rock salt, and then suspended it in a solution of sodium chloride. The crystal grew or diminished in size according to whether the solution was slightly supersaturated, or slightly unsaturated. The concentration of the solution was kept constant by addition of salt or water, and the slow development of faces by the sphere was noted. Ultimately a polyhedron developed. The speed of growth of the various faces was found. They did not all develop at the same rate.

Bound up with the formation of crystals, is the dissolution of crystals. It is of interest to know how a crystal is attacked by a solvent; whether certain faces disappear first, or whether the crystal dissolves as a whole. Little work appears to have been done in this direction, although Traube has shown that dissolution takes place at definite points on the crystal surface, and a cellular structure is thereby formed. Immediately before the crystal dissolves it breaks down into particles which are so small that they can be seen only under the ultra-microscope (§ 352). In this work, a cinematograph film was taken showing the process of dissolution. The results are considered to be in agreement with Smekal's theory that a crystal is made up of blocks of a few molecules, called "lattice blocks", which are separated by canals or pores. When a crystal dissolves it first breaks up into these blocks. This theory has been used also to explain the contamination of crystalline substances by impurities derived from the mother liquor. It is a well-known fact that crystalline substances are frequently impure, and this is a matter of importance when dealing with precipitates in quantitative analysis. Precipitates such as barium sulphate frequently contain adsorbed impurities which are difficult to wash out. It may be that these are adsorbed in the hypothetical pores which exist in the crystal. The hygroscopic nature of some crystals has also been ascribed to the same cause, water being adsorbed in the pores. *

With reference to the effect of impurities on crystals, it may be mentioned that in some instances crystals reject impurities. For example, many dyes are not taken up by crystals, and it is possible to crystallise a colourless substance from a solution that has been artificially coloured by certain dyes. This is not always so, however, and if an impurity can form a solid solution with the crystal, or, if it is adsorbed in the pores, it is a matter of some difficulty to remove it.

Sometimes the crystalline form of a solid may be completely altered by the presence of impurities in the solution from which it is deposited.

It is possible to obtain cubes of alum although the usual crystal habit is octahedral.

Recent work indicates that crystals grow in discrete layers. These layers may be a few molecules deep or they may be some hundreds of molecules or ions deep. The various faces of a crystal grow at different rates. The formation of a layer starts not on the edge of the crystal as might be expected (because the surface forces would be greatest at the edges) but at the centre of a face. Once a layer begins to form it tends to be completed before the next layer starts forming. From this it appears that each layer requires a fresh initiation of crystallisation; that is a fresh nucleation; and that the rate of crystallisation depends on the rate of nucleation at a crystal surface.

132. Supercooling and Amorphous Substances.—It has already been stated that when a melt is cooled it frequently does not crystallise without the presence of dust particles, or crystallites (small crystals) of the substance to be crystallised, or mechanical agitation. A liquid in this condition is said to be supercooled. The way in which the presence of dust particles causes precipitation is not known. The other methods of bringing the melt to crystallise can be given some theoretical explanation. The presence of crystallites actually provides the nuclei, whilst mechanical agitation provides further opportunities for the molecules of the liquid to come into those arrangements from which crystalline nuclei result.

Supercooling is most frequently found with viscous liquids. When such a liquid is supercooled its already high viscosity gradually increases, and, of course, this means decreased motion of the molecules, since the internal friction is increased. Hence, as supercooling proceeds, the chance of crystal nuclei appearing becomes less and less, and a glass (which actually is still a liquid) is frequently produced. This flows like a liquid, though, of course, very much more slowly, owing to the much increased viscosity, and no new phase appears during the cooling.

A typical example of a supercooled liquid is ordinary glass. It flows, as can be seen if a piece of glass rod or tubing is supported on two pegs, about a metre apart, when it will soon show a permanent sag. Old glass, too, will crystallise out when rendered slightly less viscous by warming, making it useless for glass-blowing. This process is known as devitrification.

Many substances, especially when thrown down as precipitates, appear to show no definite crystalline form to the naked eye, or even under the microscope. These are usually called amorphous substances. It has now been shown that almost all substances previously thought to be amorphous, are in fact microcrystalline, or else are liquids. Thus the so-called "amorphous" phosphorus (red phosphorus) has been found to consist of minute crystals, invisible to the naked eye, and not shown even under the microscope, but definitely indicated by X-ray diffraction

(§ 134). The question is not, however, definitely settled. Some maintain that the amorphous state should be regarded as a fourth state of matter. Recent work has shown that certain metals can be obtained in thin layers (by vaporisation and subsequent condensation, or by other methods) in such a form that they are almost non-conductors of electricity. X-ray investigation of these layers (§ 139) shows them to possess no definite crystalline structure, and they are probably amorphous.

Sometimes a precipitate is obtained in a gelatinous form when two reactants are mixed. For example, the precipitate of aluminium hydroxide, when ammonia is added to a solution of aluminium chloride, is gelatinous, and troublesome to filter. On examination by the X-ray method it is found to possess no definite crystalline structure. When, however, the hydroxide is obtained as a powder by prolonged warming with ammonia it shows a crystalline structure. It is clear that the gelatinous aluminium hydroxide cannot be called a supercooled liquid, so these results seem to provide evidence for the existence of a separate amorphous state. As already stated (§ 129) Riley and his school have obtained truly amorphous carbon.

133. Crystal Systems.—It is necessary to have an idea of the elements of crystallography in order to study crystals. Only the merest outline can be given here. For more detailed study text-books of crystallography should be consulted.

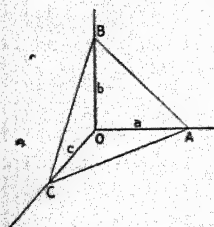


FIG. 74.—Intercepts, a , b , c , made on the axes OA , OB , OC .

Although crystals of a given substance may vary in size, and in the development of the different faces, due to variations in the method of preparation, the angles between the faces are always the same. This is called the *law of the constancy of interfacial angles*.

If three convenient axes are taken in the crystal, say three axes mutually at right angles, the faces will cut these axes at definite points (Fig. 74). The distances of these points from the point of intersection of the axes, O (called the origin), are called intercepts. The second law of crystallography is concerned with these intercepts. It is found that if the axes are suitably chosen, the intercepts of the faces upon them bear a simple ratio to each other, or particular faces may cut an axis at infinity (i.e., the face may be parallel to the axis). This is called the *law of rationality of intercepts* (or indices), and will be illustrated below. It forms the basis of a system of nomenclature for the crystal faces.

A crystal is made up of an innumerable set of smaller crystals, but if broken up, a point would be reached at which the smallest possible crystal of the substance would exist. If it were broken down still further the crystal would be completely destroyed, and the molecules or other

particles which made up the crystal would be obtained. This being so, it is clear that this smallest possible crystal has the same degree of importance as the molecule.

It has been known for some time that a crystal must be made up of an ordered assemblage of units. The only way in which the crystal can be made up of these units is such that if a definite point (e.g., the centre of gravity) is taken in each unit, these points must lie on lines and planes which divide the space into a set of parallel-sided cells. The sides of these cells are parallel to the crystal axes mentioned above. The cell is called the *unit cell*, and the assemblage of points is called the *space lattice*.

The unit cell will be completely defined by the ratio of the edges, and the interfacial angle. These are shown in Fig. 75 as a , b , and c , and as α , β , and γ respectively. Of course, these figures can be determined from larger crystals. It is not necessary to measure the size of the crystal unit, for each larger crystal is made up of a number of smaller ones, and hence the ratio remains the same. An example is copper sulphate, for which the following data have been obtained:—

$$a : b : c = 0.5715 : 1 : 0.5575$$

$$\alpha = 82^\circ 16' \quad \beta = 107^\circ 26'$$

$$\gamma = 102^\circ 40'$$

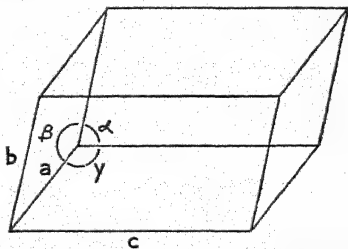


FIG. 75.—Unit cell.

It may be said that this diagram does not resemble a copper sulphate crystal. It is quite true that in external form it does not, but the method of obtaining it must be remembered. It is the unit obtained by joining the points, arbitrarily chosen, in the tiny crystals of which the larger crystal is composed, and so its shape may bear no relationship to the actual shape of the crystal, apart from the fact that its edges correspond to the crystal axes.

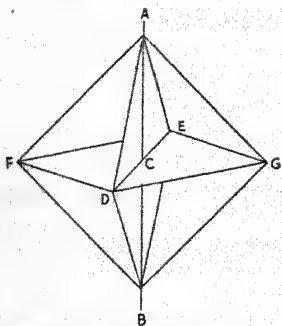


FIG. 76. — Chrome alum crystal showing two of the planes of symmetry (ADBE, FDGE), an axis of symmetry (AB), and a centre of symmetry (C).

If a crystal of chrome alum, which has the octahedral form (Fig. 76), is considered, it is seen that there are several planes of symmetry, two of which are marked in the figure.

An *axis of symmetry* is an axis about which rotation of the crystal causes it to occupy the same position more than once during the rotation through 360° . The position may be taken up twice, thrice, four times, and so on, the axis being called accordingly an axis of twofold, threefold, and fourfold symmetry, respectively.

A crystal has a *centre of symmetry* when like faces are arranged in pairs in corresponding positions on either side of this centre.

The cube has the greatest symmetry. It can readily be shown from a diagram that it has thirteen axes of symmetry (three of these are of fourfold, four of threefold, and six of twofold symmetry), nine planes of symmetry, and a centre of symmetry, making altogether 23 elements of symmetry.

Of course, only a perfect crystal shows all the elements of symmetry possible for its form. Most crystals are imperfect and have some faces better developed than others, but as mentioned before, the angles between the faces are the same whether the crystal is perfect or imperfect.

To fix a face of a crystal it is customary to define it by the intercepts it makes on certain chosen axes. Thus, in fixing the faces of the cube,

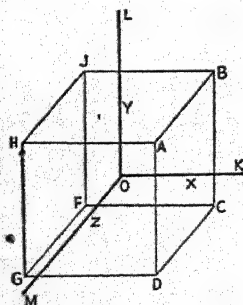


FIG. 77.

three lines mutually at right angles passing through the centre of symmetry would be chosen as axes. These are shown in Fig. 77.

The centre of symmetry is O. The three lines taken at right angles are OK, OL, OM. The line OK cuts the face ABCD at X; the line OL cuts the face ABJH at Y, and the line OM cuts the face ADGH at Z. These faces are not cut by these axes anywhere else, except when the axes are produced backwards, when they cut the opposite faces. It is clear that the intercepts OX, OY, and OZ are all equal and can therefore be taken as

unity. The faces are defined by the intercepts they make on the axes. Thus, face ABCD cuts the X axis at the point 1, the Y axis at infinity, and the Z axis at infinity. Hence this face can be represented as $(1, \infty, \infty)$. More often the reciprocals of the intercepts (called indices) are used, so that the face becomes the $(1, 0, 0)$ face. The face FGHE is similar indices to ABCD, since it is the mirror image of the latter. The plane ABJH cuts the X axis at infinity, the Y axis at 1, and the Z axis at infinity. Its name is therefore the $(\infty, 1, \infty)$ face, or the $(0, 1, 0)$ face. The face ADGH cuts the X axis at infinity, the Y axis at infinity, and the Z axis at 1. It is therefore the $(\infty, \infty, 1)$ face, or the $(0, 0, 1)$ face.

In this way the faces of any crystal can be defined. The axes chosen for the calculation need not be axes of symmetry, though they are

usually chosen thus. It has been found that these indices are always small numbers, below 7.

The octahedron (Fig. 78) may be taken as another simple example. Take, as before, three axes mutually at right angles passing through the centre of symmetry C. Since the triangles which make up the faces of this figure are all equilateral, the intercepts CX, CY, and CZ are all equal. The face AXY is therefore the (111) face. In fact, all the faces of the octahedron have these same indices.

It has been found that all crystals can be referred to seven different types of structure. They are all modifications in one way or another of seven simple types. These, together with their axial characteristics and elements of symmetry, are given in Table XXXIII. The fact that there are seven types of crystal structure does not mean that there are only seven different kinds of crystal form. Few substances exist in the simplest forms; there are usually a number of extra faces. Thus, the octahedron belongs to what is called the cubic system, because it has the same type of axes as the cube.¹

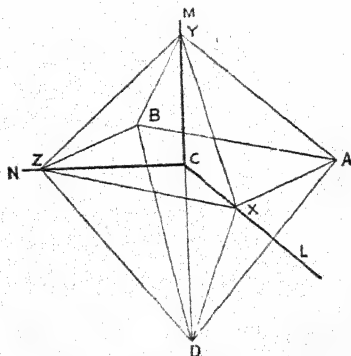


Fig. 78.

134. The Structure of Crystals.—

When light falls on an object which is of the same order of size as the wavelength of light, it does not form a perfect shadow, but is diffracted. This fact is usually investigated by means of a diffraction grating, which consists of a number of very fine lines drawn on metal or some other material. When monochromatic light falls on a diffraction grating, the light is diffracted and a number of images are formed, called the first, second, third, etc., order images. The fine lines act as small obstacles in the path of the light and cause it to be diffracted. For further information on this point, the text-books of physics must be consulted.

In 1912 Laue suggested that if X-rays were actually light of very small wavelength, and if crystals were made up of orderly arrangements of atoms or molecules, then the crystal should act as a diffraction grating for X-rays. This orderly arrangement is the crystal lattice, or space lattice. The spaces between the molecules in a crystal had been roughly computed to be about 10^{-8} cm., and this is of the order of the wavelength of X-rays. The crystal would not be such a simple diffraction grating as the type used in physics. It would, of course, be a three-dimensional grating. However, the fundamental effect, it was thought,

¹ Good photographs of crystals of the various systems are given in "Inorganic and Theoretical Chemistry", F. Sherwood Taylor (Heinemann).

TABLE XXXIII.—CRYSTAL SYSTEMS

System.	Axial characteristics.	Symmetry.	Substances typical of system
1. CUBIC . . .	Three equal axes at right angles.	Nine planes. Thirteen axes.	Sodium chloride. The alums. Diamond. Many metals. Fluorspar.
2. TETRAGONAL . . .	Three axes at right angles, two only being of equal length.	Five planes. Five axes.	Potassium ferro-cyanide. Zircon. Rutile. Tinstone.
3. ORTHORHOMBIC . . .	Three axes at right angles, but all of different lengths.	Three planes. Three axes.	α -Sulphur. Iodine. Potassium nitrate. Barytes.
4. TRIGONAL . . .	Three axes not at right angles, but of equal length and making equal angles with each other.	Three planes. Four axes.	Quartz. Graphite. Sodium nitrate.
5. HEXAGONAL . . .	Three axes of equal length in one plane, making angles of 60° with each other, and a fourth axis at right angles to them, and not of the same length.	Seven planes. Seven axes.	Lead iodide. Magnesium. Beryl.
6. MONOCLINIC . . .	Three axes of unequal length, one at right angles to the other two, which are inclined at an angle not 90° .	One plane. One axis.	Potassium chlorate. Borax. Sodium carbonate. Gypsum. β -Sulphur.
7. TRICLINIC (or anorthic).	Three axes of unequal length, all inclined at unequal angles, not a right angle.	No planes. No axes.	Copper sulphate. Potassium dichromate. Orthoboric acid. Microcline.

would be the same. Laue showed, from a theoretical point of view, that if a beam of X-rays were to fall on a crystal, it should be transmitted through the crystal as a number of diffracted beams. If a photographic plate were arranged directly behind the crystal, these beams should

make their appearance on the plate as a number of spots. From a consideration of the position of these spots it should be possible to arrive at some conclusions about the positions of the molecules in the crystal.

The experimental work in connection with this was carried out almost immediately by Friedrich and Knipping. Their results agreed com-

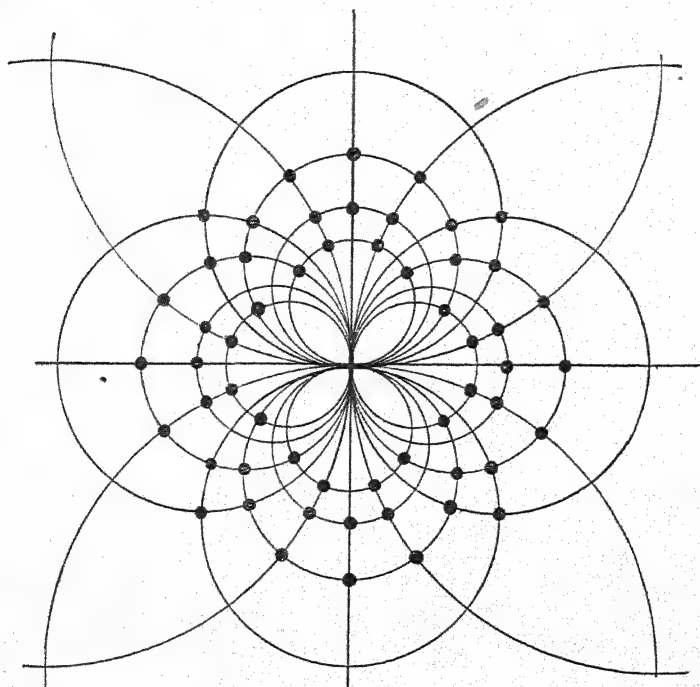


FIG. 79.—Theoretical Diffraction Pattern for Sodium Chloride.
(After Fig. 8, from Dr. E. S. Hedges' *Chapters in Modern Inorganic and Theoretical Chemistry* (Edward Arnold & Co.).)

pletely with the predictions of Laue. The points are found at the intersection of circles, which represent the diffraction at the various planes. Fig. 79 shows the theoretical X-ray diffraction pattern of rock salt.

This method did not receive a great deal of attention, since at the time little was known about the nature of X-rays and the arrangements of atoms and molecules in crystals, although this research did much to increase our knowledge on both these points. The method has, however, been used very extensively since.

A little later Sir W. H. and W. L. Bragg suggested that a crystal should be used as a reflection grating rather than as a transmission grating. The arrangement of atoms or molecules in a crystal is such that the atoms and molecules may be regarded as occurring in planes which are fixed by the symmetry of the crystal. The faces of a crystal

are parallel to these planes containing the atoms or molecules, and those faces which occur most frequently are developed parallel to those planes in the space lattice which contain the largest number of atoms or molecules. When X-rays fall on these planes they are reflected, and the resultant reflected beams interfere with each other, just as when a beam of light falls on a pile of glass plates, as in the echelon grating. The theory of this is very easily followed.

In Fig. 81 the lines aa' , bb' , cc' , dd' , etc., represent the planes of atoms or molecules parallel to a face of the crystal. According to our hypothesis,

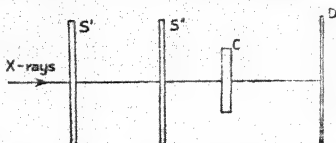


FIG. 80.—Diagram to illustrate the Laue experiment. X-rays are passed through pin-holes in the lead sheets S' and S'' , then through the crystal C . The beam is diffracted and a number of images of the pin-holes appears on the plate D , their positions being defined by the intersection of circles of radii dependent upon the distances between the lattice planes.

these planes are all parallel and are equidistant. Suppose that the distance between them is d . W represents an advancing wavefront. The first plane is struck at A , and the wave is there reflected along AB . The angle WAa is equal to the angle $BAA' = \theta$. Part of the beam, however, is reflected at the second plane, at the point E , part at the

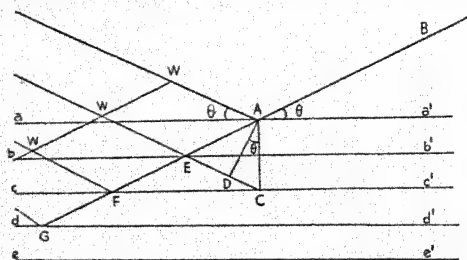


FIG. 81.

third plane, and so on. The line WE is produced to C . The perpendicular to the crystal planes from A must meet it at C . AD is drawn perpendicular to EC . From the geometry of the figure it is clear that the angle $DAC = \theta$. The beam which emerges from the crystal along AB is made up of a number of beams which have travelled through the crystal for different distances, and therefore will be out of phase unless the path is a finite integral number of wavelengths different. Thus, for reinforcement, the path difference must be an integral number of wavelengths; for interference the path difference must be an odd number of half wave-

lengths. We wish to express the first of these conditions mathematically.

The path difference of the waves taking the courses WA and WE is

$$EA - ED = \Delta.$$

But,

$$EA = EC.$$

Therefore,

$$EC - ED = DC = \Delta$$

But,

$$DC = AC \sin \theta = 2d \sin \theta,$$

where d is the distance between successive planes.

For maxima, Δ must equal $n\lambda$, where λ is the wavelength and n is an integer. Hence the condition for maximum reflection is

$$n\lambda = 2d \sin \theta.$$

It is clear that it is necessary to know λ and θ to find d . n is known from the order of the spectrum, or, if monochromatic light is used, the order of the reflection. The first reflection is obtained when $n = 1$. At first the wavelengths of X -rays were not known, so that it was necessary to express the distances between the planes in the crystal lattice in terms of λ . This was, of course, suitable for comparative work, but not until the wavelengths of the X -rays were found was it possible to give an absolute measure of the lattice constants.

The apparatus used by the Braggs for the investigation of crystals was very much like an ordinary spectrometer in principle, and is shown in Fig. 82.

X -rays are generated from the X -ray tube A , and are made as far as possible monochromatic by passing through absorbing screens S , after which they pass through lead slits L , to obtain a fine beam. The beam passes on to the crystal face, the crystal being mounted on a turntable which can be moved over a scale V , very much as a diffraction grating is mounted in ordinary spectroscopy. The reflected beams are passed into an ionisation chamber D , which is connected with an electrometer. The ionisation chamber can also be moved over a circular scale independently from the crystal. The chamber contains some easily ionisable gas, such as sulphur dioxide, and when the gas is ionised by the rays a reading is obtained on the electrometer. The crystal face and the ionisation chamber are rotated about their common axis, the chamber being rotated through twice the angle through which the crystal is turned. In this way the angle between the face and the ionisation chamber, and the face and the

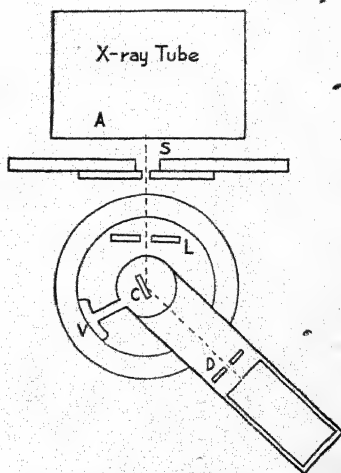


FIG. 82.— X -ray Spectrometer.
(Bragg.)

incident beam, are kept the same. The strength of ionisation produced at different angles, as measured by the current indicated by the electrometer, is determined and plotted, and from the graph the maxima are obtained.

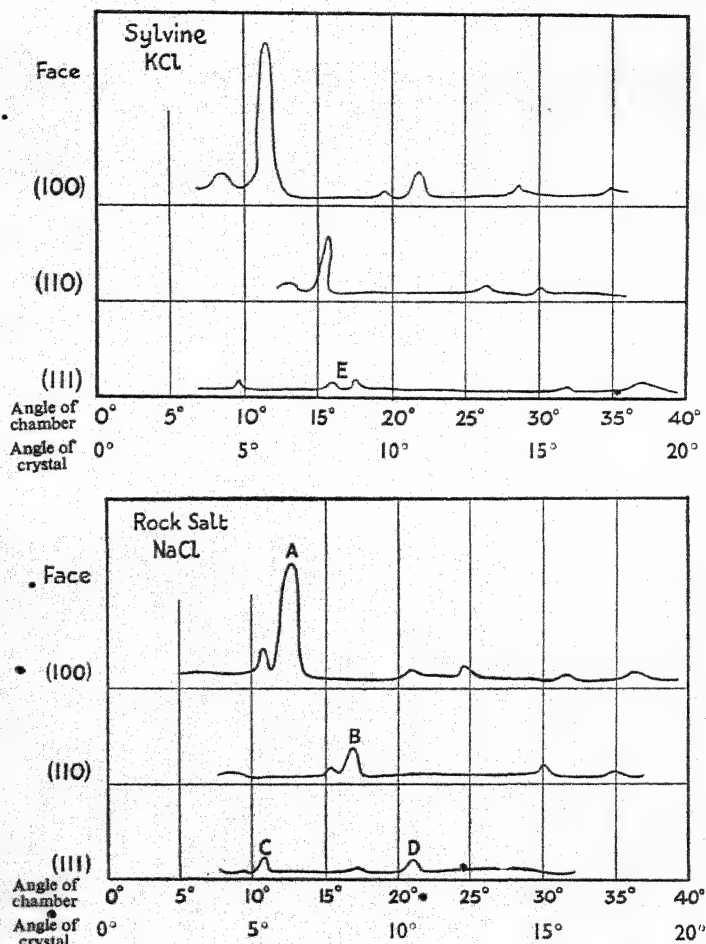


FIG. 83.—Intensity of X-ray Reflections and Angle of Setting of Ionisation Chamber for Sylvine and Rock Salt (Bragg).

These maxima should be governed by the equation

$$n\lambda = 2d \sin \theta,$$

so that, since d and λ are constant for any one face, the ratios of $\sin \theta$ should be small whole numbers.

The curves obtained for potassium chloride (sylvine crystals) and sodium chloride (rock salt) are given in the accompanying figure. The angles given in the top scale of Fig. 83 are the settings of the ionisation chamber, and are equal to 2θ , where θ is the angle through which the crystal is turned.

For sodium chloride, the maximum reflections for the (100) face occurred at $\theta = 5.9^\circ$, 11.85° and 18.15° for palladium X-rays. The sines of these angles are 0.103, 0.205 and 0.312, which are very nearly in the ratio 1 : 2 : 3. This speaks for the truth of the relationship deduced above.

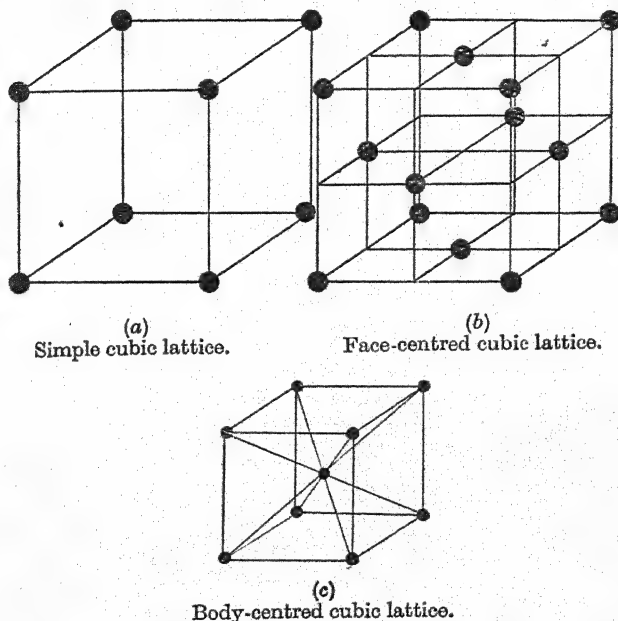
(a)
Simple cubic lattice.(b)
Face-centred cubic lattice.(c)
Body-centred cubic lattice.

FIG. 84.—Types of Cubic Lattice.

These figures enable the distance between the planes in the space lattice parallel to this face to be calculated. In the equation

$$n\lambda = 2d \sin \theta,$$

when $n = 1$, $\sin \theta = 0.103$. Hence

$$\lambda = 2d (0.103) \quad \therefore d = 4.85\lambda.$$

Thus we have the distance between the reflecting planes of particles parallel to the (100) face in terms of the wavelength of the rays used.

In order to find the absolute spacing, it is necessary to decide to which system the crystal belongs, and then to calculate the relative

distance between the planes in the different types of lattice that are possible for the different faces. These are compared with the results of the X-ray analysis, and the correct space lattice is thus arrived at. Once this is done, the absolute spacing can be derived from a knowledge of the density of the crystal and Avogadro's number. The crystal could then be used as a means of determining the wavelength of X-rays, just as an ordinary diffraction grating is used for the determination of the wavelength of light.

These points are clearly brought out in the study of the crystals sylvine and rock salt. These were the first crystals that were successfully studied by the Braggs, and they are comparatively simple. It is well known that they both crystallise in the cubic system, for which there are three space lattices possible, which are called the simple cubic, the face-centred cubic, and the body-centred cubic lattices. These are shown in Fig. 84.

The simple cubic lattice has one structural unit, whatever that may be in the crystal under consideration (molecule, atom or ion), at each corner of the cubic cell. In the face-centred lattice there is a structural unit at each corner, and one at the middle of each face of the cell, whilst in the body-centred lattice there is one unit at each corner, and one at the centre of the cube. Sylvine and rock salt may crystallise in one of these three ways. The relative spacings between the planes containing structural units, and which act as reflection planes for the rays, are now calculated. The possible crystal faces are (1) parallel to the cube face (100), (2) perpendicular to the diagonal of the face (as in the faces of a dodecahedron) (110), and (3) perpendicular to the cube diagonal (as in the octahedron) (111). The relative spacings are given in the table below, and should be verified by the student.

TABLE XXXIV

Type of Lattice.	(100).	(110).	(111).
Simple cubic	1	$\frac{\sqrt{2}}{2}$ (.707)	$\frac{\sqrt{3}}{3}$ (.577)
Face-centred cubic	1	$\frac{\sqrt{2}}{2}$ (.707)	$\frac{2\sqrt{3}}{3}$ (1.154)
Body-centred cubic	1	$\sqrt{2}$ (1.414)	$\frac{\sqrt{3}}{3}$ (.577)

Consider the curves obtained for the intensity of reflections against the angle of setting of the ionisation chamber (Fig. 83). For sodium chloride, we see that the first order reflections occur at the following angles of crystal face for the different faces

A	(100)	5.9°
B	(110)	8.4°
C	(111)	5.2°

It must be remembered that small deviations in the curve cannot be counted as reflections, and that the maxima will occur at double these angles if we consider settings of the ionisation chamber, since this has to be moved through twice the angle that the crystal is turned through in order to receive the reflection. To make this clear, the first order maxima are marked in the diagram with the letters A, B and C. The sines of these angles and other data are given in the table below.

$$n = 1$$

$$d = \frac{n\lambda}{2 \sin \theta}$$

TABLE XXXV

Face	(100)	(110)	(111)
Angle (θ)	5.9°	8.4°	5.2°
$\sin \theta$	0.103	0.146	0.094
d	4.854 λ	3.425 λ	5.319 λ
Ratio of d	1	0.706	1.096

These ratios of d obviously agree with the face-centred cubic lattice, and with no other, so it is clear that in rock salt the ultimate crystal cell has its structural units arranged in a face-centred manner. The difficulty now arises as to what the structural unit is. If it is the NaCl molecule, presumably there will be some distance between the two atoms in the molecule, and we may associate the centre of gravity of the molecule with the points of the lattice. Thus, the Na and Cl atoms will actually lie on two face-centred cubic lattices, which are separated from each other by a definite distance (the distance between the atoms in the molecule), and interpenetrate. The same result is arrived at if we associate the sodium atoms with the points of the lattice. The chlorine

atoms will, as before, lie on a similar interpenetrating lattice. However, it is now universally regarded that the units are sodium and chlorine ions, not atoms. The problem now is to find the position of these two face-centred cubic lattices with respect to each other. The clue to the solution of this problem is found in the intensity of the various order reflections. The X-rays are scattered by the structural units, and the amount of scattering will be proportional to the mass of the scattering particle. The heavier the atom (or structural unit, whatever it may be) the greater will be the intensity of the reflection. The chlorine is considerably heavier than the sodium, so that the reflections will be mainly due to it, those due to sodium being much weaker.

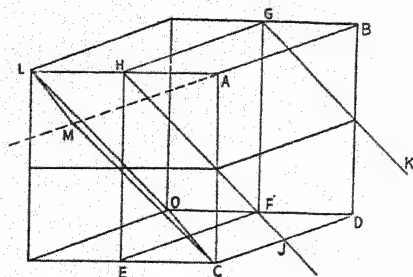


FIG. 85.—Diagram showing the planes referred to in the text.

The planes $ABCD$ }
 $EFGH$ } are (100) planes.

The plane $GHJK$ is a (110) plane.

The plane $LMCO$ is a (111) plane.

Note that these are alternately made up of sodium and chlorine ions, and are half as far apart as they would have been if the sodium and chlorine ions had not been arranged in this manner.

It is found that if it is supposed that the chlorine space lattice is displaced from the sodium space lattice half-way along the side of the fundamental cube, the results shown in the reflection curves are accounted for. The type of lattice thus obtained is shown in Fig. 86. It is noticed that the sodium and chlorine ions alternate. The lattice is now made up of eight simple cubic lattices, but containing two kinds of ion. The planes parallel to the cube faces contain the same number of chlorine and sodium ions, and the spacing is identical with the original fundamental space lattice. This is also the case for the (110) planes. However, the original (111) planes are now alternated with planes containing sodium ions only at half the distance between the original planes. It is obvious that the presence of these planes will interfere with the reflections from the (111) faces. For the reflections from the two successive chlorine planes to reinforce each other, the path difference must be one wavelength. When this is so, any rays reflected from the sodium planes will have travelled odd numbers of half wavelengths, and

so will be 180° out of phase. If the reflections from the chlorine and sodium planes therefore were equal in intensity, there would be no reflection at all at this angle. However, the sodium is not so heavy as the chlorine, and consequently the reflections from the chlorine planes are more intense than those from the sodium planes, and there is a resultant effect, though it is much weaker than it would otherwise be. This is true for the first order reflection, and explains why this is extraordinarily weak. For the second order reflection the waves from the sodium planes would be one wavelength behind those from the preceding chlorine planes, and so there would be reinforcement. For the third order reflections, however, we have similar conditions to the first, the waves from the sodium planes being one and a half wavelengths behind those from the preceding chlorine planes. This agrees with the intensities obtained. In Fig. 83, C is the first order, D the second order, whilst the third order spectrum is not sufficiently intense to mark.

When a crystal of potassium chloride is considered, it is found to possess a similar lattice to that of sodium chloride, but here the first order spectrum for the (111) face has entirely disappeared. This is easily explained on the above basis. The atomic weights of chlorine and potassium are not very different, and hence the intensity of X-rays reflected from them will be approximately the same. Here the waves will neutralise each other completely for the first and third order reflections, whilst they will reinforce each other for the second, giving a more powerful reflection of the second order, shown at E, Fig. 83.

It is interesting to carry the investigation further and find the exact distance apart of the planes. This can be done if the dimensions of the unit cell can be found. It has already been

seen that the elementary cell of the sodium chloride crystal consists of a chlorine ion at each corner, and one at the centre of each face. Each atom at a corner of the cube really belongs at the same time to seven other cubes, so that only one-eighth of its mass may be regarded as belonging to the elementary cell. There are eight of these atoms, so that the resultant total mass of atoms at the cube corners is 1. Every atom in a cube face is shared with another cube, so that it gives half its mass to any particular elementary cell. There are six of these, so that they give the mass of three ions altogether to the elementary cell. The total number of chlorine ions is therefore four. It can be shown in a similar way that the number of sodium ions in the cube is equivalent to the mass

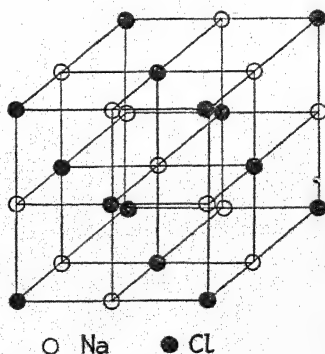


FIG. 86.—Sodium Chloride Lattice.

of four.* The cell therefore contains four molecules of sodium chloride. The density of sodium chloride crystals is 2.17 gms. per c.c., and the molecular weight 58.454. The gram-molecular volume is, therefore, $58.454/2.17 = 26.93$ c.c. This must contain a number of molecules equal to Avogadro's number, *i.e.*, 6.06×10^{23} . The volume associated with four molecules will be

$$4 \times \frac{26.93}{6.06 \times 10^{23}} = 177.8 \times 10^{-24} \text{ c.c.}$$

This must be the volume of the unit cell. The cube root of this gives the length of the side of the cube, and this comes out to be 5.623×10^{-8} cm. One Ångström is 10^{-8} cm., so that the length of the side is 5.623 Å. The distance between the (100) planes is half this, *i.e.*, 2.811 Å. The other distances can be calculated in a similar way. Knowing this distance between the planes, it is clear that the crystal can now be used to determine the wavelength of the X-rays used.

The X-ray spectrograph differs from the X-ray spectrometer just described in fixing the positions of the maximum reflections photographically instead of by an ionisation chamber. The Laue method is a typical one involving the spectrograph. The arrangement of apparatus for this method has already been described, and the type of photograph explained. The spectrographs are easily obtained if a good crystal is available, but the interpretation of the diagrams is not easy, and is usually accomplished by means of gnomonic projection. The method cannot be described here. Laue photographs find their main use in the determination of the symmetry and correct unit cell of a crystal. Qualitative data are obtained from complicated planes far more numerous than in any other diffraction methods, and these can be employed with great certainty in the fixing of the unit cell.

135. X-Ray Powder Spectroscopy.—Debye and Scherrer (1916) and Hull (1917) suggested that a powder might be used instead of a large crystal in X ray spectroscopy. If the crystal is replaced by a thin film of crystalline powder an entirely different pattern is formed. If the small crystals are present in large enough numbers and if they are arranged in a disordered fashion, two conditions which are almost invariably fulfilled, there are bound to be some of them which are in a position to reflect from every system of atomic planes whose spacing is more than a certain minimum, fixed by the wavelength of the X-rays used.

The substance is powdered and made into a rod and placed at the centre of a circular camera. The beam of X-rays, after suitable treatment by slits, is passed through a hole in the photographic film on to the specimen. The X-rays are diffracted in such a way as to give a series of cones with their apices at C (Fig. 87). Where they cut the film, the circular sections of the cones will be made evident. When the

film is unrolled the photograph is of the form shown in Plate Ib., which is the photograph obtained for $C_{22}H_{46}$. It will be clear from what has been said above that the apparently straight lines in this diagram are really portions of arcs.

Each line in this photograph arises from comparatively few crystals—just those in fact which are oriented in such a way as to reflect the rays from one particular plane—and so they will be much weaker than the spots in the Laue diagram unless a considerably more powerful source of rays is used.

This method has certain advantages over the other methods. Crystals can be studied which it is not possible to grow to a large size. Whereas it is difficult to grow large crystals of most substances, anything can be finely powdered. The intensities of the reflections are used besides their positions to obtain the size of the unit cell.

136. The Rotating Crystal Method.

—This was devised by Rinne, Schiebold, and Póányi, and has been used extensively in determining crystal structure. A monochromatic beam of X-rays, suitably defined by slit arrangements, falls on a crystal which is rotated about an axis perpendicular to the beam. The reflections are recorded on a circular film, as in the powder method.

In some work, the crystal is rotated only through a small arc, in other experiments the crystal may be rotated through 360° . It is best to use a single crystal, as perfect as possible, but very small specimens may be employed. Good photographs are obtained by this method, but the work involved in deciding the structure from a study of the photographs is considerable. A typical rotation photograph is shown in Plate Ic.

137. X-Ray Grating Spectrographs.—It has been mentioned in §134 that a crystal could be used as a diffraction grating for X-rays, and that if the lattice spacing of the crystal were known the wavelength of the X-rays could be deduced. Until quite recently this was the only method available for the determination of the wavelength of X-rays. The ordinary line grating, as used for ordinary light, could not be employed for X-rays owing to the very small wavelength. In 1930, Thibaud and Siegbahn devised X-ray spectrographs which used ruled gratings. It was not possible to rule gratings very much closer than those used in work with ordinary light, but this was compensated for by making the rays to be analysed strike the surface of the grating almost tangentially. With a very small angle of incidence, it is possible to diffract ordinary

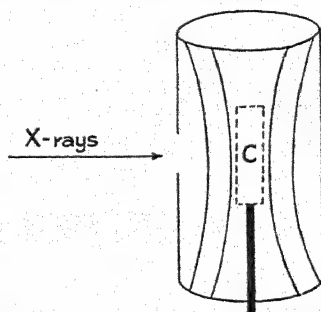


FIG. 87.—X-ray Powder spectroscopy.

X-rays with an appreciable angle, even if the grating has only 50 lines per millimetre. The results obtained with this apparatus agree with those using the crystal grating, and thus provide valuable confirmation of the earlier work.

138. Results of X-ray Analysis.—X-ray analysis of crystals has contributed largely to our knowledge of the crystalline state. In fact, we can say that we know more about the solid state than we do of the liquid state. Almost all solid substances have been shown to be crystalline, and a definite arrangement of atoms may exist even in certain liquids. Precipitates and colloids, previously thought of as amorphous, have been shown in the great majority of cases to be crystalline. The glasses, which were previously regarded as definite solids, are now thought to be supercooled liquids, and should not be treated as solids at all.

As previously mentioned, another great change in our idea of the solid state has been brought about by X-ray analysis, for it is clear that the term "molecule" now has no significance when we refer to solid salts.

X-ray analysis has also helped to elucidate the structure of organic compounds, by indicating exactly what the molecule is like and the nature of the linkages between the atoms. From a study of the crystal structures of aliphatic compounds, it has been shown that there is a tetrahedral arrangement of bonds about a carbon atom, the latter being united to four other atoms. The diamond has been shown to possess a structure in which each carbon atom is surrounded by four others, equidistant from it. This reminds one of the van't Hoff tetrahedral carbon model. The six-membered ring is also found in the diamond and graphic lattices. A study of hexa-methylbenzene and of naphthalene and anthracene shows the planar nature of the six-membered ring.

The difference in hardness between diamond and graphite also finds an explanation in the crystal structures which have been deduced for these two forms of carbon. Both have the hexagonal ring, but in the diamond there is a branching, which brings the planes of atoms closer together than in graphite. The two structures are shown in Fig. 88.

The distance between two adjacent planes in the diamond is 1.54, Å whilst in graphite the distance is 3.40 Å. The reason for this is that carbon is in an sp^3 hybridised state in diamond and an sp^2 hybridised state in graphite. As a result in diamond adjacent planes are cross-linked by covalent bonds; in graphite adjacent planes are not linked by chemical bonds but are held together by Van der Waals forces. Because of these factors diamond is a hard substance but graphite flakes easily. The bonds in the graphite hexagonal rings are 1.42 Å long which is the same as the bond length in carbon to carbon aromatic bonds. The bonds in diamond are 1.54 Å long, and this is the same as the ordinary carbon to carbon aliphatic bond length.

X-ray analysis has provided a method for investigating metals, and

the effects which take place on rolling, drawing, and heat-treatment. This work is of special value to the metallurgist. An X-ray study of steel and iron shows that when carbon is introduced into iron the large crystals of iron are broken up into a large number of small ones which interlace, and thus give to steel its strength.

Substances such as cellulose and rubber have been studied by this method. Cellulose has been found to possess a definite structure.

Vegetable and animal fibres, in general, give rise to X-ray diffraction patterns when a fine beam of X-rays is passed through a bundle, about 1 mm. thick, of parallel fibres. These are usually called "fibre-photographs". A typical photograph for Ramie fibre is shown in Plate II.

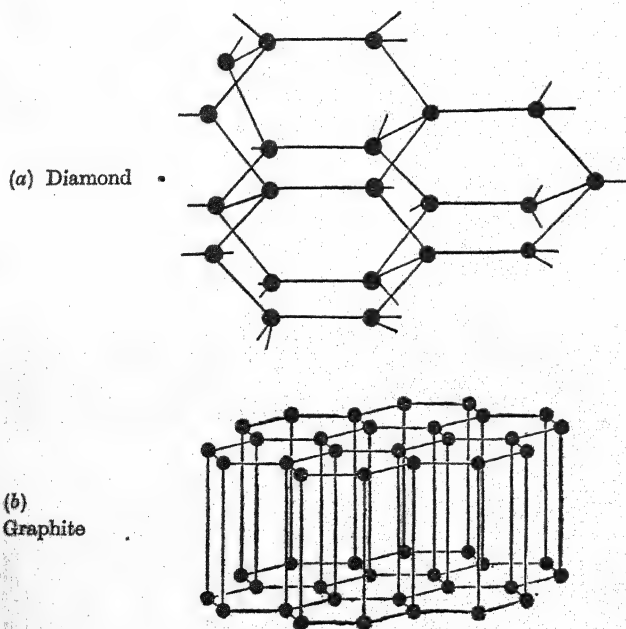


FIG. 88.—Structure of Diamond and Graphite.

[Based on diagrams in Tutton's *Crystalline Form and Chemical Constitution* (Macmillan).]

The changes which take place when cotton is mercerised have been elucidated by the aid of X-ray analysis. Rubber has been found to crystallise and decrystallise as it is stretched and slackened.

Outside the realm of purely experimental technique, the most outstanding advance in X-ray crystallography has been the mathematical treatment by Prof. J. M. Robertson of the practical data obtained by diffraction experiments. He first applied the method to the elucidation of

the structure of durene (1,2,4,5-tetramethyl benzene), and naphthalene, and since then it has been used for many other organic compounds. Since the crystal is essentially a periodic structure, the distribution of the scattering particles may be represented by a Fourier series. A Fourier analysis of the data reveals the detailed structure of the crystal and even the positions of the atoms in the molecules, the results confirming the conclusions of organic chemistry. For further information the student is referred to the original papers.¹

139. Electron Diffraction in Crystals.—The fundamental point of wave mechanics (§ 67) is that moving electrons are associated with a wave-motion. As has been pointed out, in 1924 de Broglie showed on purely theoretical grounds that this should be so, and stated that the wavelength λ of the motion would be given by $\lambda = h/mv$, where h is Planck's constant and mv the momentum of the particle. When this formula is applied to the case of moving electrons the wavelengths of the wave-motion associated with electrons which have fallen through potential differences of 10, 100, 1,000, and 10,000 volts, are found to be 3.86, 1.22, 0.386 and 0.122 Å respectively. If these wavelengths are compared with the wavelengths of X-rays, we find that they correspond roughly with very soft, soft, hard, and very hard X-rays. In 1925 Elsasser suggested that if de Broglie were correct, a beam of electrons should be diffracted at a crystal surface just as X-rays are. Davisson and Germer tested this with a plate of nickel. During the course of their work, their apparatus was, by accident, broken, and air entered. On repeating the work, the reflexion from the nickel was found to have altered, and this was ascribed to a change in the crystalline state of the surface of the metal. They then experimented with a single crystal of nickel, allowing a beam of electrons to fall normally on the surface, and they found that the beam was not diffusely scattered, as the classical theory predicted, but that de Broglie's theory was true. A diffraction pattern was obtained which, if the wavelengths calculated by de Broglie were assigned to the electron beams, obeyed Bragg's law. The work of many other observers in this field has also confirmed this.

It is obvious that this discovery provided another method of attacking the problem of the structure of crystals, and some very important results have been obtained with it. Electrons have not the penetrating power of X-rays, and their action is confined to the first layer comprising a few tens of molecules. It is thus a very suitable method to employ for the investigation of thin films, where the X-rays scattered from these films could not be detected. G. P. Thomson has carried out a number of experiments in this direction.^{*} Pure copper does not give diffraction rings, but on exposure to air for a short time the rings due to

¹ References will be found in *British Chemical Abstracts* (now *British Abstracts*), 1933 onwards. The number of papers published on this method is too great for detailed references to be given here.

cuprous oxide are produced. Similar oxide films were found on iron. The method has been applied to the study of "passivity". When a piece of iron is dipped into concentrated nitric acid, it becomes passive, and is unattacked by the acid, and on removal from the nitric acid it is unattacked by other reagents for some time. Two views have been held as to the reason for this. One states that an oxide film is produced, the other that an inert allotropic form of the element is formed. The former is the favoured view. If such a film were produced, it was thought that it should be indicated by this method of investigation, but it was found that no diffraction rings were produced. This is probably due to the fact that even a beam of electrons would not indicate a monomolecular film, such as the film of oxide may well be. It may, of course, not be crystalline at all, but amorphous, a view which is supported by the fact that the film of oxide which forms on aluminium when it is allowed to stand in air does not show any rings. The question is therefore left unsolved.

There is, however, a wide field available for this method of investigation, for our knowledge of thin films is very incomplete, and they are important in the study of metal corrosion, of plant and animal fibres, of fats on the surface of liquids, and of adsorbed gases. The fact that electron beams possess heating powers also makes this method useful for studying the changes in crystalline structure which take place at high temperatures.

The results of structure experiments carried out by the electron diffraction method agree closely with those obtained by the X-ray methods. The method has been applied for finding the structure of platinised asbestos. Platinisation probably results in a splitting of the fibres. Davisson and Germer have investigated the structure of gold, tungsten, molybdenum and cobalt by this method, using electrons of high speeds. Their results agree with the ordinary X-ray observations.

140. Ionic and Covalent Radii.—Atoms and ions in a crystal are assumed to be spheres. When a bond between two atoms or ions is formed it is assumed also that the bond length (from centre to centre) is equal to the sum of the two radii of the spheres; the actual radii, however, depend on the type of bond.

From a study of the diamond lattice the radius of a carbon atom when it is covalently linked by single bonds to four other atoms can be determined. It is half the C - C bond length and so is 0.77\AA . Knowing this figure it is possible to determine the covalent radii of atoms such as nitrogen (0.74\AA), oxygen (0.74\AA), fluorine (0.72\AA), and many others, by measurement of bond lengths in the appropriate carbon compounds.

The covalent radius of an atom is shortened when the atom is linked by a double or triple bond to a neighbouring atom. For example the covalent radius of carbon when singly linked is 0.77\AA ; when doubly

linked 0.67Å; and when triply linked 0.60Å. In a conjugated system the radius will have neither the single, double nor triple bond value but will be of an intermediate length, which depends on the degree of conjugation in the system considered. Thus the carbon covalent radius in benzene is 0.71Å, which is between the carbon double bond (0.67Å) and the carbon single bond (0.77Å) values. (See also § 83.)

In ionic bonds the link is always between two different atoms; so in the calculation of ionic radii there is no starting point, such as the determination of the radius of carbon from the length of the C - C covalent bond. Hence the values of two radii have to be assigned from other considerations. Once these values have been assigned it is possible to draw up a table of ionic radii from the study of the bond lengths of a number of different combinations of ions. In ionic bonds it is found that the charge has an important effect on the radius of ions. In compounds containing ions with a co-ordination number of six and having a similar electronic structure such as Na^+ , Mg^{++} , Al^{+++} and Si^{+++} the corresponding radii are 0.95Å, 0.65Å, 0.50Å and 0.41Å respectively. These show a decrease in radius with increasing positive charge. This decrease is to be attributed to the tendency of the positive charge to draw the electron shell inwards. The opposite effect is observed in negatively charged ions, thus O^{--} has radius 1.40Å, F^- 1.36Å while the radius of F when covalent is 0.72Å. The increasing negative charge is associated with an increase of radius.

The applications of ionic radii to explain Fajans rules is clear. The smaller a cation the more intense its field and hence the greater its polarising power, that is its power to deform neighbouring electronic shells. The larger an anion on the other hand the more polarisable it will tend to be, i.e., its electron shell is more affected by neighbouring cations. The result of this is that a covalent bond will tend to form between a small highly charged cation and a large anion; this is because the electron shell of the anion is attracted by the positive charge of the cation leading to a sharing of electrons between them. An electrovalent bond is formed between a large cation and a small anion. Here there is little pull on the electrons of the anion and therefore little tendency for the electrons to be shared between the ions (see § 79).

The radii are greatly increased when atoms are not linked together. For example in graphite the distances between carbon atoms in different layers is 3.25Å, so the corresponding radii are 1.625Å. Thus from measurements of distances between atoms it is possible to find whether those atoms are linked together or not. The radii may also be used to distinguish covalent and ionic bonds. In a series of covalent compounds which have the same atomic number (i.e., the same total number of electrons), the sum of the covalent radii is constant. This does not hold for ionic bonds.

Another instance in which ionic radii are important is in the packing

of ions in a crystal. Here anions are packed around cations and vice versa. The co-ordination number of a particular ion (the number of ions that can be packed around it) will depend on the ratio of the radius of the ion to the radius of the ions packed around it. This radius ratio is an essential factor in determining the lattice type in which a particular ionic compound crystallises. Other factors influencing crystal structure are the ease of deformation of the electron shells or the power of deformation that the components possess, and the repulsive forces between ions of like charge. The latter is especially important for compounds containing a very small cation, e.g., lithium; in this example the anions packed around lithium are very close together and the repulsive forces between them affect the crystal form.

141. Lattice Energies.—Three forces act upon an ion in a crystal lattice. Two of these forces are attractive in nature: these are the ordinary electrostatic force between oppositely charged ions (which decreases with the square of the distance) and the van der Waals force of attraction. The third force is the inter-atomic repulsive force which falls off very rapidly with distance. The three forces are in equilibrium in the crystal and the energy of an ion plotted against interionic distance gives a curve similar to that shown in Fig. 89. The minimum point in the curve represents the interionic distance of minimum energy and hence maximum stability. Actually ions vibrate about this mean distance. The potential energy is considered to be zero when the ions

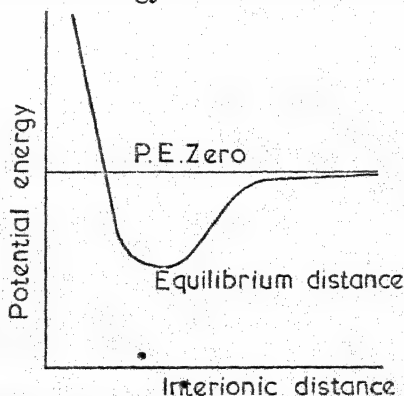


FIG. 89.—Curve of potential energy against interionic distance.

are separated by an infinite distance. The decrease in potential energy brought about by the formation of the crystal is equal to the lattice energy, which is the decrease in energy which results in the bringing of the ions from infinite separation to the positions they occupy in the crystal. The lattice energy can also be defined as the energy of formation of the crystal from one mole of gaseous ions. It is equal and opposite to the energy of dissociation of the crystal.

As the interionic distance is shortened from the equilibrium distance the repulsive forces increase very quickly and therefore the compressibility of a crystal should be small. Similarly the thermal expansion will take place against cohesive forces and will be small if these are large. The alkali metals have the greatest compressibility and the greatest thermal expansion among the solid elements. Here the cohesive forces are at a minimum. Atomic volumes and melting points also depend on cohesive forces; large cohesive forces are associated with small atomic volumes and high melting points.

142. The Specific Heats of Solids.—Dulong and Petit suggested in 1819 that the atomic heat (specific heat multiplied by atomic weight) of all solid elements is equal to about six. Many elements appear to conform to this rule, e.g., lithium 6.4, aluminium 5.7, arsenic 6.2 and silver 6.0. There are, however, many exceptions to the rule, e.g., boron 2.5, and carbon (diamond) 1.35. The Dulong and Petit rule was extended to compounds by Kopp. He stated that the molar heat of a compound is approximately equal to the sum of atomic heats. If we consider a compound made up of elements the atomic heats of which are about 6, then if n is the number of atoms in the compound, the molar heat is about $6n$. Kopp's rule of the additivity of atomic heats is a fairly accurate one.

The atomic heat of an element may be calculated on a classical basis in a manner similar to the calculation of the specific heat of gases. One gram atom of an element contains N atoms. A solid is made up of a lattice of atoms and each atom is vibrating about a mean position. The vibration can take place in three directions and each mode of vibration has two degrees of freedom (see § 123), so for each atom there are six degrees of freedom. Each degree of freedom contributes energy $\frac{1}{2}kT$ and the energy of one atom is $3kT$ and for one gram atom is:

$$3NkT = 3RT \text{ (because } k = \frac{R}{N} \text{)}$$

therefore

$$E = 3RT$$

$$\text{and } C_v = \left(\frac{\delta E}{\delta T} \right)_v = 3R = 5.96$$

This gives C_v . Most measurements of heat capacity are taken at constant pressure; there is, however, a general equation (deduced thermodynamically) which for any substance at temperature T gives the relationship

$$C_p - C_v = \frac{TV\alpha^2}{\beta}$$

where V is the atomic volume, and α the coefficient of thermal expansion and β the coefficient of the compressibility of the substance. Thus experimental measurements of C at constant pressure can be converted to C_v . For most metals C_v lies between 5 and 6 at ordinary temperatures.

which agrees with the value deduced above and with the Dulong-Petit law.

According to the classical theory C_v should be independent of temperature. Actually atomic heats are found to increase with increase in temperature. For example, the atomic heats of elements which are exceptions to the Dulong and Petit law increase as the temperature is raised, e.g., the atomic heat of carbon at 808° is 5.54 (see Fig. 90). To deduce from this, however, that the Dulong and Petit law is a limiting law is incorrect; the atomic heats of many substances which appear to obey it at ordinary temperatures rise with increasing temperature.

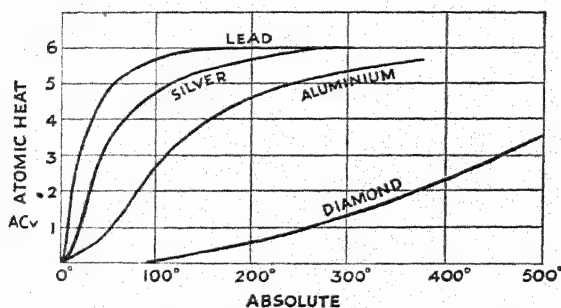


Fig. 90.—Curve showing variation of atomic heat at constant volume with absolute temperature for lead, silver, aluminium and diamond.

A quantum mechanical treatment of specific heats can now be given. As in the classical theory each atom is supposed to be vibrating about its mean position in three directions. The oscillation of each atom is assumed to be independent. Solving the wave equation of an oscillator which is oscillating in one direction, shows that vibrational energy is quantised according to the equation

$$E_v = (v + \frac{1}{2})h\nu$$

where ν is the frequency (seconds⁻¹) and v an integral number known as the vibrational quantum number. This expression gives the possible energy levels available to the vibrating atom. The distribution of the various oscillating atoms about these energy levels is found by using the Maxwell-Boltzman statistics. According to the Maxwell-Boltzman distribution the number of atoms (n_v) having energy E_v is

$$n_v = \frac{1}{\beta} e^{-E_v/kT}$$

where β is a constant.

If the total number of atoms is N and we consider only oscillation in one direction, then N is found by summing the number of atoms in each level over all the levels.

$$N = \sum_{v=0}^{v=\infty} n_v = \frac{1}{\beta} \sum_{v=0}^{v=\infty} e^{-\epsilon_v/kT}$$

$$\therefore \beta = \frac{1}{N} \sum_{v=0}^{v=\infty} e^{-\epsilon_v/kT}$$

The total vibration energy of the N atoms is the sum of the number of particles in each level multiplied by the energy of the level and summed over all levels. That is

$$E = \frac{1}{\beta} \sum_{v=0}^{v=\infty} \epsilon_v e^{-\epsilon_v/kT}$$

Using the expression for β derived above gives

$$E = N \frac{\sum_{v=0}^{v=\infty} \epsilon_v e^{-\epsilon_v/kT}}{\sum_{v=0}^{v=\infty} e^{-\epsilon_v/kT}}$$

In a crystal three directions of oscillation are possible for each atom; hence

$$E = \frac{3N \sum_{v=0}^{v=\infty} \epsilon_v e^{-\epsilon_v/kT}}{\sum_{v=0}^{v=\infty} e^{-\epsilon_v/kT}}$$

Substituting $(v + \frac{1}{2}) h\nu$ for ϵ_v gives

$$E = \frac{3N h\nu \sum_{v=0}^{v=\infty} (v + \frac{1}{2}) e^{-(v + \frac{1}{2})h\nu/kT}}{\sum_{v=0}^{v=\infty} e^{-(v + \frac{1}{2})h\nu/kT}}$$

This expression becomes

$$E = \frac{3N h\nu \sum_{v=0}^{v=\infty} (v + \frac{1}{2}) e^{-(v + \frac{1}{2})h\nu/kT}}{\sum_{v=0}^{v=\infty} e^{-(v + \frac{1}{2})h\nu/kT}} + \frac{3}{2} N h\nu$$

The last term represents the zero point energy of the crystal (the first term is equal to zero when T is equal to zero).

$$\text{As } \frac{\sum_{v=0}^{v=\infty} v e^{-v h\nu/kT}}{\sum_{v=0}^{v=\infty} e^{-v h\nu/kT}} = \frac{1}{e^{h\nu/kT} - 1}$$

$$E = \frac{3N h\nu}{e^{h\nu/kT} - 1} + \frac{3}{2} N h\nu$$

and

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v = 3Nk \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

This expression for the specific heat was first derived by Einstein. (It may be pointed out, however, that his derivation took no account of zero point energy.) At low temperature the expression approaches zero but at high temperatures when $h\nu$ is much less than kT the expression tends to $3R$ in agreement with the classical theory and the Dulong and Petit law. The Einstein equation agrees well with experiment except at very low temperatures where the calculated values fall more rapidly to zero than do the experimental values.

Debye accounts for the atomic heat of solids by assuming that a gram atom is made up of $3N$ coupled oscillators instead of N independent oscillators each vibrating in three directions. This means that the various atoms are not oscillating with only one frequency but with a range of frequencies. The actual expression derived for the atomic heat is a complicated one. At low temperatures the Debye expression becomes

$$C_v = 77.93 \times 3R \left(\frac{T}{\theta} \right)^3 \quad S. 54$$

i.e., the specific heat varies with T^3 . θ is a quantity known as the characteristic temperature; it equals $\frac{hc\omega_m}{k}$ where ω_m is the maximum

frequency of oscillations of the atoms in the crystals. As pointed out above the expression holds only at low temperatures. T must be less than $\frac{\theta}{10}$ and this is usually less than 20° K. Measurements have

confirmed the Debye equation and it is used to calculate heat capacities at low temperatures when experimental values are being extrapolated to zero degrees K. This is important in the determination of entropy.

θ can be calculated from the elastic constants of the solid and when this is compared with θ derived from specific heat measurements the agreement is good.

143. Polymorphism.—Many solid substances exist in more than one modification. In fact, it is now correct to say that this is a general phenomenon, as it is known that the great majority of substances exist in more than one form. This phenomenon is called "polymorphism", although it is customary in the case of elements to use the term "allotropism", or "allotropy". There is no essential difference between these two terms, though "polymorphism" does not cover the allotropy of non-crystalline substances, such as oxygen and ozone, ortho- and para-hydrogen, active and ordinary nitrogen, and others.

Polymorphism is due primarily to differences in crystal structure, giving rise to differences in physical properties, such as density. If a substance will crystallise in more than one crystalline form, the two forms are polymorphs. Thus a substance may crystallise in the cubic system, in one form, whilst it may also crystallise in the triclinic system,

thus providing a new form. Mercuric iodide is an example. When mercuric iodide is first precipitated it is yellow, but immediately changes to red. If the red form is heated to 126°C ., it changes into the yellow form, which on cooling reverts to the red form. The latter crystallises in the tetragonal system as octahedra, whilst the yellow form crystallises in the orthorhombic system as plates. Salts such as cupri-mercuric iodide show the effect even better. This salt changes from red to black on heating to about 70°C ., the reverse change taking place on cooling. Silver mercuric iodide changes from a buff colour to yellow at about 40°C ., and changes back on cooling.

144. Energy Content of Polymorphs.—Since polymorphism owes its existence to differences in crystal structure, or to differences in the number of atoms which go to make up a molecule, it is clear that the polymorphs will have differing energy contents. The amount of energy contained by a substance will clearly be dependent upon the positions of the molecules in the space lattice, and their relative motion will be dependent upon the crystal forces. According to the second law of thermodynamics (§ 112), no change can take place spontaneously unless it is accompanied by a decrease in the free energy of the system. Consider again the case of mercuric iodide. The transformation of the yellow form into the red which takes place spontaneously is a typical example of such a process. The second law, then, states that this change cannot take place unless there is a decrease in the free energy of the system. It follows that the less stable form has the greater energy, and the more stable form is produced from it with loss of energy. When the unstable yellow form of mercuric iodide is transformed into the stable red form, energy is given out in the form of heat, and this energy must be supplied (by means of a Bunsen burner, or some other source of heat) if it is desired to convert the red form back into the yellow.

This, then, is a special case of a general theorem. Any spontaneous change is accompanied by a decrease in the free energy of the system. Certain cases of allotropic change are examples of spontaneous changes.

The fact that the energy of the stable form is less than that of the unstable form gives rise to differences in the vapour pressure of the forms. Vapour pressure is dependent upon the escape of molecules from the crystal lattice. When the molecules possess sufficient energy to vibrate in the lattice violently enough, they escape from the lattice, forming vapour. The vapour pressure of a solid is therefore some indication of the energy possessed by the molecules. It would be expected that the more stable form possessing less energy, and the molecules being therefore unable to vibrate with as great violence, would possess the lower vapour pressure, and the less stable form the higher vapour pressure. This is found to be true.

It would also be expected that the form possessing less energy, *viz.*, the stable form, would be less reactive chemically, and this is usually so.

The differences in vapour pressure of various forms of the same substance give considerable information as to the stability of the forms.

It was mentioned above that there was a spontaneous transformation of the less stable, or labile, form into the more stable form. This does not always start itself, but requires some sort of a send-off. Many such examples are known. Thus, mercuric iodide may be kept for some time in the yellow form without returning to the red, but when it is touched by a rod, or scratched, it changes at once. Sulphur may be kept in the monoclinic form for some time, but if it is rubbed, the change to rhombic takes place rapidly. Substances which are in the labile state when the surrounding conditions are such that they would ordinarily be in the stable state, are said to be in the metastable condition. Many substances are capable of remaining in the metastable condition for a very considerable period, and particularly is this true of metals. In an English winter the ordinary form of tin is usually metastable. There are three forms of this metal, two of them being white tin and grey tin. The former is stable above 18°C ., and the latter below this temperature. Hence, whenever the temperature falls below 18°C ., as it frequently does in winter time, tin in its usual form is metastable. Tin articles have been known to change to grey tin in severe winters. Grey tin has a considerably smaller density than that of white tin (5.7 and 7.28 respectively), so that the change is accompanied by expansion, and the article usually falls to a powder. Such a change is commonly referred to as tin plague. It is related that when Napoleon marched his men out of Russia in 1812 the temperature was so low that the change from white to grey tin took place fairly easily, and the tin buttons and medals of the soldiers crumbled away.

As the temperature in this country is quite frequently below the temperature at which the one form of tin changes into the other, tin often becomes metastable and remains in the white form, although it should be converted into grey tin. If this change did occur, tin would be almost useless as a metal.

The temperature at which two forms of a substance become equally stable is called the transition temperature. It is the temperature at which both forms possess the same vapour pressure, and the same solubility, and may obviously be obtained by finding the point of intersection of the vapour pressure, or solubility curves. At a temperature slightly below this, one form becomes metastable and passes into the other, whilst at a temperature slightly above it the reverse change takes place. The transition point of the two forms of tin referred to above is 18°C ., whilst that of the two forms of mercuric iodide is 126°C .

Table XXXVI gives the transition points of various systems.

145. Types of Allotropy.—The distinction between various types of allotropy rests upon differences in the way in which the transition of one form to the other can be brought about.

In the first place, there are substances, the two (or more) forms of which are converted into each other at a definite temperature, the transition point. Examples of this type have already been given (mercuric iodide, tin). When the substance is heated it changes from form A into form B, and the reverse change takes place on cooling. This is an example of a reversible transformation, and this type is called *enantiotropy*. It is well illustrated by the examples already given, to which may be added sulphur, the details of which are given in the table and in § 146.

Secondly, transformations are known which proceed at all temperatures in one direction. There is no definite transition point. The transformation of ozone into oxygen is a good example of this class. This is called *monotropy*, and is a case of irreversibility. Thus ozone breaks down into oxygen at all temperatures, but a reversal of the process by which the change was started does not lead to the re-formation of the ozone.

Thirdly, two allotropes may exist together in equilibrium. One form may be changing into the other at exactly the same rate as the reverse process is taking place. This is called *dynamic allotropy*, and is exemplified by liquid sulphur, which consists of a mixture of two forms of sulphur, designated as S_λ and S_μ , which are in equilibrium with each other, the proportions of each present being determined by the temperature.

TABLE XXXVI

Substance.	Form.	Transition Point, °C.
Sulphur . . .	Rhombic \rightleftharpoons Monoclinic	95.6°
Tin	{ Grey \rightleftharpoons White	13° ? 18°
	{ White \rightleftharpoons Rhombic	202.8°
Zinc	{ $\alpha \rightleftharpoons \beta$	174°
	{ $\beta \rightleftharpoons \gamma$	322.0°
	{ $\alpha \rightleftharpoons \beta$	184.5°
Ammonium chloride		
Mercuric iodide .	Tetragonal \rightleftharpoons Orthorhombic	126°
Silver iodide . .	Hexagonal \rightleftharpoons Regular	146.5°
Silver nitrate . .	Rhombic \rightleftharpoons Rhombohedral	160°

146. Study of a System of each Type.—(a) *Enantiotropy*.—As already stated, a good example of this is the change of rhombic into monoclinic sulphur. If the vapour pressure of the rhombic form of sulphur is determined at various temperatures, the curve AB (Fig. 91) is obtained. There is, however, an abrupt change in the course of this curve at B, the temperature here being 95.6° C., and this is due to the change of the sulphur from the rhombic into the monoclinic form. In accordance with expectations, the vapour pressure of this form is

greater than that of the rhombic. At higher temperatures still, in the neighbourhood of 120°C ., there is another abrupt change in the vapour pressure curve, and at this point the monoclinic form is converted into liquid. If the curve is continued it represents the vapour pressure of liquid sulphur, and ultimately a point will be reached at which the liquid boils, i.e., the vapour pressure becomes equal to the superimposed atmospheric pressure. The curve can then be continued to the critical point (see § 159).

If now the conditions are reversed, and liquid sulphur is cooled from its boiling point, the vapour pressure follows the curve DC. It is possible to make the vapour pressure continue along the curve to E, without suffering any abrupt change at C. This happens when the liquid is supercooled, and no solid separates out. If, however, supercooling is prevented there is an abrupt change in the direction of the vapour pressure curve at C, and the monoclinic form is produced—this being the stable form at this temperature. As this is cooled the curve CB is followed, and as in the case of liquid sulphur it is possible to supercool this form somewhat, no rhombic sulphur being formed. If this is so the curve BF is followed. If not the curve BA is retraced.

Obviously this is an enantiotropic system, for the changes are completely reversible, and there are definite transition points.

Enantiotropic changes are also characterised by the fact that the transition points of the solid forms lie below their melting points. The melting point of the rhombic form will be given by the point of intersection of the vapour pressure curves of the rhombic form and the liquid form; it is shown on the curve as the point E. The transition point of rhombic and monoclinic sulphur, i.e., B, lies below the melting point of the rhombic form G and that of the monoclinic form C.

(b) *Monotropy*.—Another class of substances exhibiting polymorphism is that in which the change from one crystalline form to the other is not reversible. It is possible to pass only in one direction. The reason for this is that the melting point lies below the transition temperature of the two crystalline forms. Examples of this type of polymorphism are furnished by the compounds iodine chloride, ICl , and benzophenone. Each of the crystalline forms of these substances has its own melting point, those of iodine monochloride being 13.9°C . and 27.2°C . and those of benzophenone 26°C . and 48°C . In each case the transition point lies above the melting point.

If a vapour pressure—temperature diagram is drawn to represent

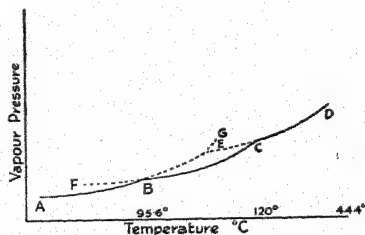


FIG. 91.—Vapour Pressure Curve of sulphur (enantiotropic System).

this type of system a graph of the form shown in Fig. 92 is obtained.

The curve AP_2 is the vapour pressure curve of the stable form, II, of the substance. At the temperature represented by P_2 the substance melts and passes into the liquid state, of which the vapour pressure curve is P_2B . The corresponding vapour pressure curve for the metastable form is CP_1 . This form melts at P_1 , and the curve, P_1B is the vapour pressure curve of the liquid. The actual transition point of the two crystalline forms would be P_3 , the point of intersection of the vapour pressure curves of the two forms, but as this is above the melting point of both forms it is never reached.

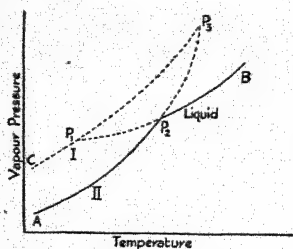


FIG. 92.—Vapour Pressure Curve for a Monotropic System.

(c) *Dynamic Allotropy*. — Certain allotropic forms of elements are capable of existing together in a state of equilibrium. There is no question of a transition point. The proportion of any one form present at equilibrium is dependent upon the temperature, and sometimes upon the pressure.

The best-known example of this is the allotropy of the two liquid forms of sulphur, S_λ and S_μ , which coexist in ordinary molten sulphur. These forms

differ in molecular complexity. This type of allotropy can only exist when the forms involved are miscible, or partly so.

147. Enantiotropy and Monotropy Combined.—It is possible for the two types of allotropy—enantiotropy and monotropy—to exist in the same system, if the substance concerned can exist in more than two crystalline forms. Sulphur is a case in point. It can exist in eight different crystalline forms, but of these the only two which show the relationship of enantiotropy towards each other are the rhombic and monoclinic forms. All the other forms are metastable with respect to rhombic and monoclinic sulphur, even up to the melting point, i.e., their transition points lie above the melting point, and they are therefore monotropic.

148. Methods of determining Transition Points.—There are several methods by which transition points may be determined, though in any particular case it is usually found that one presents many advantages over another. Besides their use for investigating the transition of one allotropic form into another, many of these methods are applicable to the study of equilibrium between salt hydrates (§ 220).

Thermometric Method. It may be regarded as a general rule that, when one phase changes into another, heat is either absorbed or liberated. Thus, if water is gradually heated, its temperature slowly rises until the boiling point is reached, when it remains stationary until all the water has boiled away. This is due to the fact that heat is taken up in causing

the change of state—the latent heat of evaporation. Similarly, if water is cooled, its temperature gradually decreases until the water starts to freeze, when it remains constant. When all the water is converted into ice the temperature again falls.

The same considerations affect the change of phase which takes place at the transition point. If a substance is cooled from above the transition point, when the transition point is reached the temperature remains constant, or may actually appear to increase a little if any considerable supercooling takes place. This is well shown by the figures obtained in the cooling of iron. If iron is cooled from its melting point and the difference in temperature between a platinum wire cooling with it, and the iron itself, is noted at different temperatures, and the results are plotted, a curve is obtained similar to that shown in Fig. 93.

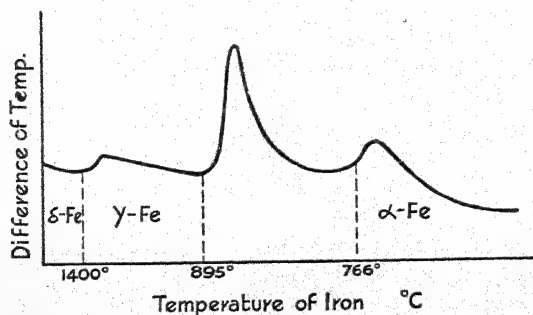


FIG. 93.—Cooling Curve for Iron.

As one form of iron changes into another, there is an evolution of heat, causing the ascents in the curve. From the melting point down to 1,400° C. a form of iron known as δ -iron is stable. Little is known about it. From 1,400° C. to 895° C., γ -iron is the stable form. Where the δ -form changes over to the γ -form there is an evolution of heat, not very large, but sufficient to cause a slight hump in the curve. γ -iron is the form in which iron usually crystallises from its alloys. It has the power of forming solid solutions with carbon. At 895° C. γ -iron changes into α -iron, and here there is quite a large evolution of heat. This was the first of these transition points to be discovered, for the amount of heat evolved is much greater than at the other transitions. If a piece of iron heated to 1,000° C. is allowed to cool, the amount of heat given out at this temperature is sufficient to cause the iron to glow, and hence the phenomenon has been termed *recalescence*. γ -iron has no magnetic properties. At 766° C. the α -form becomes magnetic. α -iron is the principal constituent of wrought iron.

Dilatometric Method. When one allotropic form changes into another there is usually a change in volume. To determine the transition point

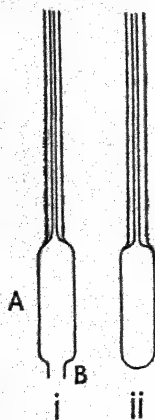


FIG. 94. — Dilatometer. (i.) Unsealed, (ii.) sealed.

it is necessary to determine the temperature at which this change in volume occurs. This can be done by means of the dilatometer, an instrument somewhat like a thermometer in design, but having a larger bulb. Originally, the instrument is made of the form shown in Fig. 94, i. The bulb A has not yet been sealed off. It is connected to a capillary tube, backed by a scale. The substance to be examined is introduced into the bulb A through the tube B, which is then sealed off. A liquid which does not act chemically on the substance to be examined is introduced into the tube, so that it covers the solid, and reaches a level on the scale. The apparatus is now gradually warmed in a bath, of which the temperature is noted. At each reading of the temperature, the height of the liquid in the tube is noted. Up to a certain temperature (the transition point), the liquid will rise uniformly in the tube, as there is uniform expansion of liquid

and solid, but at the transition point there will be an increase in volume of the solid due to change in its form, and hence an additional rise of the liquid in the tube. After this the expansion is once again uniform. On cooling, the reverse series of changes takes place.

Usually there is a certain lag in the expansion or contraction, and the curves obtained for the two cases are shown in Fig. 95. The curve ABCD is the heating curve; the curve DCEF is the cooling curve. If there were no lag, the portions of the curve indicating a rapid increase in volume would coincide. It is obvious that they do not. The correct transition point is the mean of the temperatures indicated by the two processes.

Another method of using the dilatometer is to fill the bulb with a mixture of the two forms, the transition point of which is to be determined. If the instrument is now placed in a bath, the temperature of which is exactly the transition point of the two forms, they will not be altered in any way, and consequently there will be no change in volume. If an expansion is found, the temperature of the bath is altered until there is a slight contraction. The transition point lies between these two temperatures, and can be determined by careful adjustment of the temperature of the bath. The method was used by Reicher (1884), to determine the transition point of rhombic and monoclinic sulphur. A mixture of the two forms was placed in the bulb, and a mixture of 1 part of carbon disulphide and 5 parts of turpentine was used as the indicating liquid. The results obtained are summarised in Table XXXVII.

It will be noticed that at 95.1°C . there is a contraction. Since the specific volume of monoclinic sulphur is greater than that of rhombic sulphur, this signifies a transformation of the monoclinic into the rhombic form. At 96.1°C . there is an expansion, showing that the reverse change is taking place. At 95.6°C . there was practically no

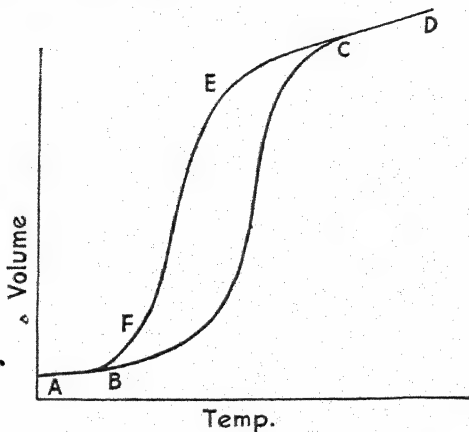


FIG. 95.—Dilatometer Curves.

change. The dilatometer in this experiment was sealed, and the pressure developed was about 4 atmospheres. The value of the transition point obtained must be corrected if the value at atmospheric pressure is required.

Measurement of Vapour Pressure. It has already been noted that the vapour pressures of allotropic forms are different, but it is obvious that at the transition point they become the same. If, then, the temperature at which the vapour pressures of two allotropic forms become identical can be determined, this will be the transition point. The simplest method of determining the vapour pressure of a solid is by means of a tensimeter. One form of the apparatus (illustrated in Fig. 96) consists of two bulb tubes connected to the limbs of a U-tube. The U-tube is filled with some manometric liquid such as pump oil. If it is desired to find the vapour pressure of a salt hydrate, some of the hydrate is placed in the bulb *d*, and concentrated sulphuric acid in *e*. The necks *d'* and *e'* are then sealed off. The instrument is now placed on its side so that the liquid in the U-tube runs into the bulbs *a* and *b*, and it is exhausted by a pump connected at *f*. After complete exhaustion, the neck is sealed at *f*. The apparatus is now set up vertically in a thermostat, and the differences in the levels of liquid in the U-tube noted. The vapour pressure of the sulphuric acid may be taken as zero, hence the difference indicated is a measure of the vapour pressure of the

TABLE XXXVII¹

Temperature, 95.1° C.

Time, mins.	Level of Liquid, mm.
5	343.5
30	340.5
55	335.75
65	333

Temperature, 95.6° C.

Time, mins.	Level of Liquid, mm.
5	368.75
100	368
110	368.75

Temperature, 96.1° C.

Time, mins.	Level of Liquid, mm.
5	342.75
30	354.75
55	360.5
60	361.5

salt hydrate. Observations are made at various temperatures.

When dealing with allotropes, one form may be placed in one bulb and one in the other. Both bulbs are heated to the same temperatures, and when their vapour pressures become equal there will be no difference in level in the U-tube. At this temperature both substances are equally stable, i.e., the temperature is the transition temperature.

All the usual methods for determining vapour pressure can be used also for these measurements, but the one described is the most convenient.

Change in Solubility. At the transition point, the solubility of the

¹ This table is taken from A. Findlay, *The Phase Rule* (Longmans), 1923, p. 284. The student is referred to this book for further details of the determination of transition points.

two forms becomes the same. The method is, however, usually employed for determining transition points between salt hydrates. Thus, if the solubility of ordinary crystalline sodium sulphate is plotted, it is found that there is a distinct break at 32.383°C . At this temperature sodium sulphate decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, is converted into the anhydrous salt, which has a solubility curve altogether different from that of the hydrate. The temperature at which the break occurs is the transition point between these two forms (Fig. 97).

Ammonium nitrate exists in five different crystalline forms. In each case there is a different solubility curve. The form known as β -rhombic

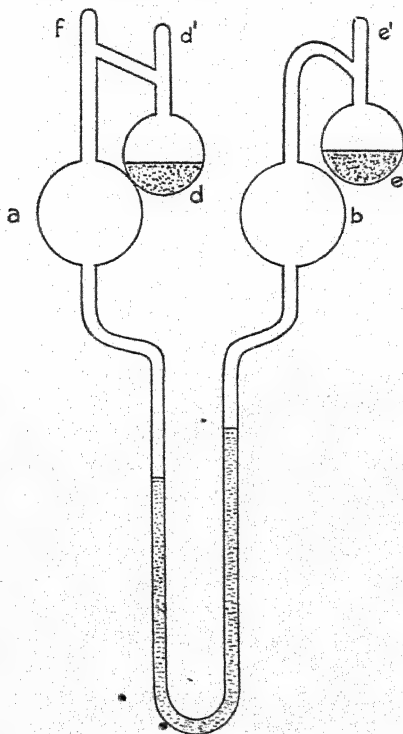


FIG. 96.—Tensimeter.

passes into γ -rhombic at a temperature of about 32°C ., and so there is a break in the solubility curve at that point (Fig. 98). The point where the break occurs is really the point of intersection of two separate solubility curves, and at that point both forms have the same solubility.

Optical Methods. Sometimes there is a visible alteration in one form when it changes into another. Thus the colour changes of the mercuric

iodide complex salts, and of the mercuric iodide itself, can readily be observed, and the temperature at which the change takes place is the transition point. Changes in crystalline form, when unaccompanied by changes in colour, may be observed under the microscope. Also, changes in the refraction of crystals can be thus observed.

Electric Methods. When a metal is placed in a solution of one of its

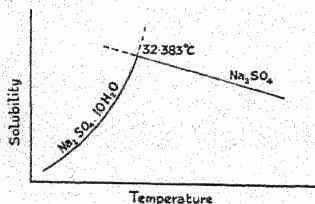


FIG. 97.—Solubility Curve of Sodium Sulphate.

salts, there is a potential difference between the metal and the solution. The amount of this potential difference depends upon the form of the metal, and the concentration of the solution. If, therefore, an electrical cell is made up of a metal, say tin, with one electrode of one allotrope and the other of the other allotrope, placed in a solution of a

salt of a metal, say ammonium stannichloride, the cell will possess a certain electromotive force (E.M.F.), which could send a current through an external circuit. If arrangements are made to warm the cell, the two forms become equally stable and have the same potential with respect to the solution when the transition point is reached. Hence, at this temperature the cell has no E.M.F. It is thus possible to determine the transition point with accuracy. The method will be more fully understood after reading Chapter XVI.

Other Methods. The transition temperatures of some salts have been found by plotting the viscosities of saturated solutions at various temperatures. A sharp break in the viscosity curve occurs at the transition point.

•An interesting method that has been used to determine the transition point between α - and β -zinc is the resistance to indentation.

Conductivity for heat and electricity has also been used for this purpose. Indeed, it may be said that almost any physical property can be used for determining transition points, for the physical properties of allotropes or polymorphs usually differ considerably.

149. Comparison of Melting Points and Transition Points.—

(1) *Analogies.*—(a) Both transition temperatures and melting points are perfectly definite temperatures, and may be used for thermometric standards. It is usual to employ the melting point of ice as a fixed point in thermometry, but transition points are equally suitable and have frequently been proposed as subsidiary standards. Many transition points are known correct to one-thousandth of a degree. Thus, the transition point of sodium sulphate decahydrate to the anhydrous salt is known to be 32.383°C ., and has been proposed as a fixed point in thermometry.

(b) Both transition points and melting points are affected by pressure. The way in which the transition point is altered depends, like

the case of the melting point, on whether the new phase occupies a larger or smaller volume than the old. Some substances expand on transition. In this case the transition point is raised by increase of pressure. If contraction occurs on transition, increase of pressure causes a lowering of the transition point. This is an application of the theorem of Le Chatelier and Braun¹ that whenever a constraint is placed on a system in equilibrium, the equilibrium is altered in such a way as to tend to annul the effect of the constraint. The effect of an increase in pressure on a body is to decrease its volume. Consider two forms of a substance, A and B, the form A being stable above the transition point, and B below it. Suppose the two forms are existing together in equilibrium at the transition point. When the extra pressure is applied, the result is to transform the substance entirely into that form which has the smaller volume, thus tending to annul the effect of the pressure. In other words, the equilibrium condition is entirely upset, and in order to restore it the temperature must be raised or lowered. Thus, the new transition point will be either above or below the old, according to which form has the less volume.

(c) At both transition point and melting point there is an evolution or absorption of heat when passing from one phase to the other. The stable form at higher temperature always passes into that stable at lower temperature with heat evolution, a fact made use of in the determination of transition points by the thermometric method already referred to. The same applies to melting points. The reverse effect is found in the transition from a form stable at low temperatures to that stable at high temperatures. Here there is an absorption of heat. Both these effects follow from Le Chatelier's theorem. At the transition point both forms are equally stable. If the mixture of the two forms at the transition point is heated, the equilibrium will be shifted in such a way that heat is absorbed. Hence the form stable at high temperatures must be formed with absorption of heat. On the other hand, if the mixture of two forms at the transition point is cooled, that form will be produced which is stable at low temperatures, and it will be formed with evolution of heat.

(d) The addition of a second substance causes the transition point to be lowered, just as it causes a depression of the freezing point.

(2) *Differences.*—(a) Transition points usually mark the change from

¹ This theorem is sometimes referred to simply as the theorem of Le Chatelier, and sometimes as the theorem of Le Chatelier and Van't Hoff.

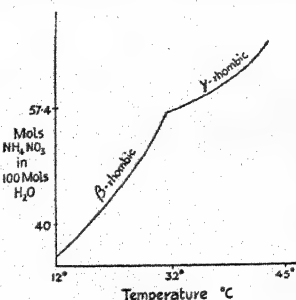


FIG. 98.—Solubility curve of ammonium nitrate.

one solid phase to another solid phase, whereas the melting point marks the transition from a solid to a liquid phase. The change in the case of transition will be considerably slower than with melting, for the movement of molecules in solids is slower than in liquids, and it will therefore take a longer time to rearrange the molecules.

(b) Arising out of this, it is clear that owing to the difficulty experienced by molecules of solids in changing their arrangement, it is quite possible to superheat a form without the transformation taking place. Thus it is possible to superheat rhombic sulphur and get no monoclinic sulphur formed. This is not possible with the melting point. It is almost impossible to superheat a solid above its melting point.

150. Study of some Common Allotropic Systems.—(1) *Sulphur*.—There are said to be more allotropes of sulphur than of any other element, but there is not the slightest doubt that many of the so-called "allotropes" are mixtures. The chief forms are:—

α -Sulphur (Rhombic or Octahedral),	
β -Sulphur (Monoclinic or Prismatic),	
Nacreous Sulphur.	
Tabular Sulphur,	
γ -Sulphur (Plastic),	
δ -Sulphur (Amorphous),	
Colloidal Sulphur,	
λ -Sulphur,	} forms of liquid sulphur.
μ -Sulphur,	
π -Sulphur (possibly)	

The allotropy may conveniently be considered under the headings:—

- I. Solid equilibria, enantiotropic changes.
- II. Crystalline solid monotropic forms.
- III. Liquid sulphur.
- IV. Colloidal systems.

I.—Ordinary α -sulphur is enantiomorphic with β -sulphur. When α -sulphur is heated to 95.6°C ., it is converted into the β -form, and when the latter is cooled it reverts to the α -form at this temperature—the transition point. The molecular formula of these two varieties is S_8 . This formula has been obtained by studying the lowering of the freezing points of certain solvents, on dissolving known amounts of the forms in them. Study of the elevation of the boiling points of these solvents, when sulphur is dissolved in them, leads to the same result (§ 282).

II.—Nacreous, or mother of pearl sulphur, was discovered by Gernez in 1884. Molten sulphur, after heating in a test-tube to above 150°C ., is cooled down to, and maintained at, a temperature of 100°C ., in a water-bath. On gently scratching the walls of the tube with a glass rod, the sulphur crystallises in the nacreous form. It can also be obtained by crystallisation of a solution of sulphur in benzene, but special conditions

must be observed. It is monoclinic, but has not the same interfacial angles as β -sulphur. This is an example of monotropy in the sulphur system, for nacreous sulphur is always metastable, changing to rhombic or monoclinic sulphur according as the temperature is below or above 95.6°C . It is, however, possible to melt nacreous sulphur at 106.8°C ., before it has had time to change into another solid form.

Tabular sulphur is said to be formed when solutions of ammonium sulphide in alcohol are oxidised at temperatures below 14°C . It is also monoclinic, but with different angles from β -sulphur. Like nacreous sulphur, it is a monotropic form.

III.—Liquid sulphur presents a difficult problem. When sulphur is heated to a temperature above its melting point it forms, at first, an amber-coloured liquid, which, as the temperature is increased, becomes darker and more viscous, until, at one stage, it cannot be poured from the tube. As the temperature is increased still further, the liquid becomes more mobile, until finally it boils. The changes in colour and other physical properties are due to the change in the relative proportions of two allotropes, known as λ -sulphur and μ -sulphur. Aten (1912-13) believed that another allotrope, π -sulphur, was also present in the liquid, but this conclusion is open to some doubt. It is now generally considered that liquid sulphur consists of the two allotropes, S_{λ} and S_{μ} , in dynamic equilibrium (Ch. X.). These two allotropes are not completely miscible, but form a sol (§ 347). The amber-coloured liquid formed when sulphur first melts seems to be pure S_{λ} , but as the temperature is increased S_{μ} is formed in increasing quantities, until, at the boiling point, the liquid is almost pure S_{μ} . S_{μ} is probably colloidal, and has a high molecular weight. From the work of West and Menzies on the thermal data for liquid sulphur, high molecular weights are to be expected, possibly as high as S_{16} .

IV.—When liquid sulphur is rapidly cooled, plastic sulphur, or γ -sulphur, is produced. The nature of this form may vary, since it will depend upon the composition of the liquid from which it is prepared. It is a rubber-like mass, and may be a gel (§ 346), since sols (liquid sulphur is a sol) often give gels on solidifying. If this is so, the continuous phase is, probably, β -sulphur, and the disperse phase μ -sulphur. The structure of plastic sulphur has been studied by Trillat and Forestier, who find that this form is not amorphous, as would be the case if it were merely a supercooled liquid like glass. X-ray examination shows that the sulphur gives a "fibre photograph", with a definite crystalline form. This may be due to the β -sulphur. These observers noted also that exposure to X-rays caused a rapid conversion of plastic into rhombic sulphur.

Colloidal sulphur itself is frequently produced in chemical reactions involving sulphur compounds. Thus, when dilute hydrochloric or sulphuric acid is added to a dilute solution of sodium thiosulphate, a

solution is obtained containing colloidal particles of sulphur. The colloidal sulphur may be coagulated by the addition of an electrolyte.

The nature of amorphous sulphur, δ -sulphur, has not yet been fully established. It may be found to be micro-crystalline. It is obtained by adding an acid to a solution of a polysulphide, such as yellow ammonium sulphide. The fact that it is soluble in carbon disulphide, like α - and β -sulphur, lends support to the view that it may be micro-crystalline.

(2) *Phosphorus*.—There are three real allotropes of phosphorus, which are named according to their colour, white, violet and black phosphorus. Red phosphorus is a solution of violet in white, whilst the so-called "scarlet phosphorus" of Schenck is merely violet or red in a fine state of division.

White phosphorus, which is the form commonly occurring, is not the stable form. The system is monotropic. There is no definite transition point between white and violet phosphorus, as the transition point lies above the melting point. When the liquid obtained from any form is cooled, it does not follow the stable curve, but passes across to the metastable, along P_2P_1 in Fig. 92. Thus white phosphorus is always formed as a result of cooling liquid phosphorus. This follows the "law of successive reactions" enunciated by Ostwald (§ 153).

White phosphorus is the metastable form, and that this is so is evident from many of its properties. It is by far the most reactive form. It therefore contains more energy than red or violet. More heat is given out in its combustion. It will glow. It has the greater vapour pressure at ordinary temperatures.

Violet phosphorus is obtained by crystallising phosphorus from molten lead or bismuth, and then dissolving away the metal electrolytically, or with nitric acid. This form has a much lower chemical activity than the white form. It does not glow, and it has a lower heat of combustion. It also has a lower vapour pressure at ordinary temperatures.

Red phosphorus is known to be a solid solution of white in violet, because of its varying properties. According to its mode of preparation, it contains varying amounts of white phosphorus, which can be removed by careful washing with water, when the violet form is left. It also varies in colour, though this may be due to variation in particle size rather than in composition of the solution.

The point to be emphasised about the allotropes of phosphorus is that they form a monotropic system, there being no transition point.

By exposing white phosphorus to great pressure at 200° , Bridgman prepared a black form of phosphorus. In properties this is similar to violet, but is a better conductor of heat and electricity.

White phosphorus appears to exist in two forms with a transition point at -77°C. at atmospheric pressure.

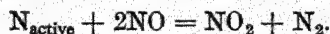
(3) *Carbon*.—There are probably only two allotropes of carbon—

diamond and graphite. At one time it was customary to call each form of charcoal an allotrope of the element, but X-ray analysis shows that some of them are microcrystalline and have the graphite structure, and therefore should not be called separate allotropes. They are probably merely graphite in a very fine state of division. This may be true of all the charcoals—or so-called “amorphous” forms—although all of them have not yet been examined.

Diamond and graphite differ in their crystalline structure, but as regards their stability there is very little difference. This accounts for the fact that transition from one form to the other is extraordinarily slow. The heat of combustion of diamond is $-7,873$ gm.-cals. per gram, whilst that of graphite is $-7,836$ gm.-cals. per gram. These figures indicate that the intrinsic energies of the two forms are almost identical, but that diamond, as it contains slightly more energy, is the metastable form at ordinary temperatures. However, the conversion of diamond into graphite has never been observed to take place spontaneously at any temperature.

(4) *Nitrogen*.—If the silent electric discharge is passed through nitrogen, a form of the gas with enhanced activity, called “active” nitrogen, is produced. This active nitrogen, as would be expected, is very unstable. It changes back to the ordinary form with the emission of light.

The chemical activity of the gas is shown by the fact that it combines directly with the vapours of many metals, giving nitrides. It reacts with sulphur at 100°C. , giving a mixture of nitrogen sulphides. It also combines directly with phosphorus and with many types of hydrocarbons. With nitric oxide, a very peculiar reaction takes place:—



The nature of active nitrogen is still unknown. As the glow is increased by cooling, and decreased by heating, it was at first thought that the re-formation of nitrogen molecules was taking place by the combination of smaller units, such as atoms. Heat would tend to prevent this. If active nitrogen consisted of atoms of nitrogen, or of molecules with the formula N_3 , it ought to be possible to liquefy the gas, but this has never been done. If, too, the gas consisted of single atoms, the amount of energy imparted by the discharge should be sufficient to cause the breakdown of the molecules to form these atoms, but calculation shows that it is quite insufficient for this task. It seems probable that energised molecules are produced by the electric discharge. Sir J. J. Thomson suggested that the outer ring of electrons, which in ordinary nitrogen contains five, may divide into four and one, thus giving a molecule with increased energy.

(5) *Hydrogen*.—It has been shown that ordinary hydrogen consists of two distinct forms which differ slightly in physical properties. Their

existence was predicted from calculations based on wave-mechanics. Hydrogen was stated to be capable of existence in two forms differing in nuclear spin (§ 71). A short time later, hydrogen was actually separated into its two allotropes, by fractional adsorption on charcoal under pressure, at the temperature of liquid air. The two forms are called ortho- and para-hydrogen, and the ordinary gas is an equilibrium mixture containing about 75 per cent. of the ortho form. As an example of differences of properties of these two forms of hydrogen, melting points may be quoted: that of para-hydrogen is 13.83° Abs., that of ortho-hydrogen is 13.96° Abs. There is also a difference in boiling point, and in specific heat. The allotropes of hydrogen must not be confused with the isotopes of the element.

(6) *Tin*.—Tin is a trimorphous metal. The upper transition temperature is 202.8° C., and the lower 18° C., though some estimates have placed the latter at 13° C. Reference has already been made to the existence of two enantiomorphous forms of tin with the lower transition point, and it was pointed out that ordinary white tin is frequently in the metastable condition in this country. The change from white to grey tin is very sluggish, but the reverse change from grey to white is not so slow, and takes place rapidly when hot water is poured over grey tin. The change from white to grey takes place much more readily when nuclei of grey tin are already present, and it therefore appears to spread by infection; hence the name "tin plague" which has been given to this change.

The transition at the higher temperature is from tetragonal to rhombic crystals. Tetragonal tin has the highest density of the three forms.

	18° C.	202.8° C.	
°	Grey tin \rightleftharpoons Tetragonal tin \rightleftharpoons Rhombic tin		
	Sp. gr.	Sp. gr.	Sp. gr.
	5.80	7.286	6.56

(7) *Antimony*.—Antimony exists in a number of allotropic modifications. Yellow, or α -antimony, is very unstable, and is formed by the action of ozonised oxygen on liquid stibine at -90° C. It changes readily into a black powder, thought to be amorphous. This in turn soon changes into the ordinary form of antimony, the rhombohedral or β -form, at ordinary temperatures. Amorphous antimony was obtained by Gore in 1858 by the slow electrolysis of a strong solution of antimony trichloride in hydrochloric acid with a platinum cathode and an antimony anode. This form is very unstable, and when scratched falls to a powder with a slight explosion. As the fumes given off in this explosion always contain antimony trichloride, it is thought that this so-called "allotrope" may be only a solution of the trichloride in black amorphous antimony.

151. Velocity of Transformation of Metastable into Stable Forms.—

It has already been mentioned that the change from one form to another does not necessarily take place rapidly. There are numerous external conditions which alter the speed at which the change takes place. Many transformations of metastable into stable forms take place with extraordinary slowness. In fact, in some cases the form of a substance ordinarily met with is the metastable form which has not changed, and shows no signs of changing, into the stable form. White phosphorus, for example, is metastable, and shows no inclination to change into red except in the light; and, as already stated, there are frequent occasions upon which white tin is metastable, and yet the sluggishness that characterises the change from white to grey tin makes it possible to preserve articles made of white tin indefinitely. Often the slowness is due to the fact that crystal forces of some magnitude have to be overcome, and bonds broken and re-made. Where the new phase has not appeared, the transformation is said to be "suspended".

It has been found that, in order to avoid suspended transformation, it is necessary to have present a small quantity of the phase it is desired to obtain. The effect of "inoculation" of a system with a crystal of the substance required from it is well known. The amount of substance required to act in this way is exceedingly small, and has been measured in the case of supercooled salol, 1×10^{-7} gms. being sufficient to bring about crystallisation. The presence of this small amount of substance provides a certain number of crystallisation nuclei, around which others form, and the whole mass crystallises.

Mechanical shock can also bring about transformation. Hence the value of stirring and scratching the sides of the vessel containing the melt in bringing about crystallisation (see § 132).

It must be understood that it is not all solids that can bring about crystallisation from a system in suspended transformation. Only the substance itself, or one possessing a very similar crystal lattice, is effective.

The velocity of crystallisation of supercooled liquids has been studied by a number of investigators. The supercooled liquids were placed in narrow glass tubes, and crystallisation was started by inoculation. The time taken for the crystallisation to get a certain distance along the tube was determined. It was found that for any given degree of supercooling the velocity of crystallisation was constant. As the degree of supercooling is increased, the velocity of crystallisation also increases up to a maximum. This maximum remains constant over a large range of temperature, after which it diminishes again, and for very severe supercooling may become zero. This is probably what has happened in the case of glass.

The velocity of transformation is affected in various ways by many other external agencies. Thus the addition of a liquid which dissolves

both forms may considerably accelerate the velocity of transformation. At the transition point, the solubilities of the two forms become equal, but at any given temperature, the solubility of the more stable form is less than that of the less stable. If two solid phases are brought into contact with a solvent which dissolves both of them, it will dissolve one form more than the other. The solution will become saturated with respect to this form, the less stable one, but is then supersaturated towards the stable form, and this is deposited. An example of this is the well-known fact that tin changes more readily from white to grey in the presence of a solution of ammonium stannic-chloride. It is necessary to state, however, that a solvent may sometimes retard the velocity of transformation, especially if it be viscous.

Temperature may affect the change. As already mentioned, the velocity of crystallisation of a supercooled melt depends upon the temperature.

Certain substances, added in small quantities to the system, may cause the change to be brought about more readily, acting in this way as catalysts. The best-known case of this is the acceleration of the change of white phosphorus into red by the addition of a very small quantity of iodine.

152. Mechanical Strains in Metals.—The question of metastability of metals has received a good deal of attention because of its great practical bearing in everyday life. The practical usefulness of many metals depends alone upon their metastability.

When copper and some other metals are stretched and rolled and hammered, their properties are considerably altered. They become harder, and their tensile strength increases. This can be shown to be due to a change of state of the metal, the new state being metastable because the metal possesses a higher solution pressure after treatment than it did before, resulting in its being more electronegative with respect to a solution of one of its salts (§ 337).

It is thought that a metal in this metastable condition is very much like glass. In the process of working, the crystals are, in part, broken down, and the substance becomes semi-amorphous. Just as glass devitrifies on heating, so the metal after treatment, when it is heated, passes from the semi-amorphous, metastable state into the crystalline stable state.

153. The Law of Successive Reactions.—It has frequently been observed that when a substance passes from a metastable into a more stable condition, it does not reach the most stable form at once, but attains it through successive stages. If sulphur vapour is cooled it is first transformed into a liquid, which solidifies in the monoclinic form and slowly changes to the rhombic. The liquid sulphur does not change at once into rhombic sulphur. White phosphorus is always formed when

phosphorus vapour is cooled, although it is in the metastable condition, and only with extreme slowness is violet phosphorus produced from it. In organic chemistry it is frequently found that a substance is deposited as an oil, which gradually undergoes solidification to crystals. The oil is not the stable form, or it would not spontaneously crystallise.

There are a very large number of these examples, and Ostwald has made the generalisation called the *law of successive reactions* to embrace them. This states that when a system passes from a less stable condition it does not pass directly into the most stable, but reaches this by traversing intermediate conditions of progressively greater stability.

There are some apparent exceptions to Ostwald's Law, but it may be taken as true in the great majority of cases.

154. Crystal Structure and Chemical Constitution.—Haüy, the founder of the science of crystallography, put forward the rule in 1784 that every definite chemical compound had its own crystalline form, but certain apparent exceptions to this statement were soon found. In the same year, it was noted that crystals of potash alum could contain a good deal of iron, and yet still retain their crystalline form. In 1816, Gay-Lussac grew a crystal of potash alum in a solution of ammonium alum, so that Haüy's Law did not appear to be correct. It seemed from this experiment that two substances had the same crystalline form, and this could not be so if Haüy's Law were true.

In 1819 Mitscherlich put forward his *law of isomorphism*, which states that *substances possessing an equal number of atoms, united in a similar way, exhibit identity of crystalline form.*

This statement makes two provisions. There must be an equal number of atoms in the molecule, and these atoms must be united in a similar way. It is obviously conflicting with Haüy's Law, for according to him there is no such thing as identity of crystalline structure of two chemical compounds. Each compound has its own structure, irrespective of whether it is similar in composition to anything else or not, if Haüy's Law is correct.

Mitscherlich's Law of Isomorphism proved so useful in various ways in the development of chemistry (see § 11) that its truth was not doubted, but more recently experiments have been carried out to see whether substances with similar chemical compositions actually do have identity of crystalline structure, and it has been found that the identity is not complete. There are minute differences in the crystal angles. No two substances have exactly the same crystalline structure. As an example, the two substances, ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and copper sulphate (Boothite), $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$, may be quoted. These two compounds are definitely isomorphous. They satisfy all the criteria of isomorphism as laid down in the next section, but, as the table shows, there are slight differences in the dimensions of the unit cells and in the angle of the cell.

	a : b : c	β
Copper sulphate, $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$.	1.1622 : 1 : 1.5000	74° 24'
Ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.	1.1828 : 1 : 1.5427	75° 44'

It is seen, then, that Haüy's Law is true, and that Mitscherlich's Law cannot be enforced too rigidly. There is another point, too, where Mitscherlich's Law has proved to be erroneous. It states that substances showing isomorphism must contain equal numbers of atoms. Now, many substances are known which are isomorphous, and yet which have not the same number of atoms. An example that comes to mind at once is ammonium alum, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, and potash alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. The ammonium alum contains eight more atoms to the molecule than does potash alum, and yet the two are isomorphous. Many other examples could be quoted.

Mitscherlich's Law, as it was first proposed, can hardly be called a law. It is therefore better to amend it, and merely say that substances which have similar chemical compositions frequently possess very similar crystalline forms. In fact, it is now known that the condition for isomorphism is similarity of the internal structure of the crystals rather than similarity of chemical properties. Isomorphous crystals contain geometrically similar units.

. 155. **Methods of Recognising Isomorphism.**—Since complete identity of crystalline structure is not strictly a criterion of isomorphism, this method cannot be used to recognise it. There are some crystals which have crystalline constants very similar to each other, yet they are not isomorphous. It is found, however, that if substances are isomorphous their crystal elements are closely similar, though the converse is not necessarily true.

The formation of *mixed crystals* is a good criterion of isomorphism. If two substances are isomorphous, it is possible to make crystals containing both of them in varying proportions. These crystals are called "mixed" crystals. As an example of their formation, copper sulphate and ferrous sulphate may be taken. If a solution containing these two substances is crystallised, it is always found that the copper sulphate crystals contain a certain amount of iron. Hence the difficulty of purifying copper sulphate by fractional crystallisation. The crystals always bring down with them some iron, and this can only be removed by treating the solution with concentrated nitric acid, which oxidises the ferrous sulphate to ferric sulphate, in which form it is no longer isomorphous with copper sulphate. It is then possible to crystallise the copper salt free from iron.

Not all isomorphous crystals are capable of forming mixed crystals.

Thus, whilst the actual formation of mixed crystals is in general a good proof of isomorphism, the converse—that if substances are isomorphous they should form mixed crystals—is not true. The formation of mixed crystals appears to be governed by the molecular volumes of the substances. If these are close there is greater probability of the formation of mixed crystals.

Another method of deciding whether two substances are isomorphous is to see whether they will form isomorphous overgrowths with each other, *i.e.*, if one crystal will grow in a solution of another. Here, again, there are some exceptions. When two substances are chosen with almost the same molecular volumes, they may form overgrowths, and yet not be isomorphous.

It will be seen that none of these criteria, *viz.*, (1) similarity of crystal-line form, (2) formation of mixed crystals, and (3) formation of isomorphous overgrowths, provides a perfectly complete test for isomorphism; but if more than one of these is found to hold good for two solids, it may usually be taken that they are isomorphous.

156. Isopolymorphism.—Substances existing in more than one crystalline form may be isomorphous in each form with another compound also existing in more than one form. An example will make this clear. Arsenious oxide occurs in two forms, one octahedral and the other rhombic. Antimonious oxide also exists in two varieties, similar in crystalline form to the arsenious oxide crystals. The octahedral forms of the two oxides are isomorphous, as are also the rhombic forms. The oxides are said to be isodimorphous. There are several cases of isodimorphism known, and a few of isotrimorphism.

Another phenomenon sometimes referred to as isodimorphism is illustrated by the behaviour of the compound iodine bromide IBr , which is isomorphous on the one hand with iodine, and on the other with bromine.

157. Applications of the Phenomenon of Isomorphism.—Mitscherlich's Law of Isomorphism finds its greatest application in the determination of atomic weights, where it serves as an aid to the fixing of valency. Examples of its application to the determination of the atomic weights of vanadium, beryllium, zirconium, silver and selenium, have already been given in the section on atomic weights (§ 11).

158. Vapour Pressures of Crystals.—Every solid substance possesses a vapour pressure, though in the great majority of cases this is very minute. The fact that solids do possess this vapour pressure is evidenced by the fact that certain solids evaporate to quite a marked extent when left out in the open, whilst many solids possess a smell, which they would not have if no vapour were given off. Like the vapour pressures of liquids, that of a solid increases with temperature. It may reach atmospheric pressure before the solid melts, in which case sublimation occurs. In sublimation, the solid evaporates without melting, and is

deposited on the cold sides of the vessel. It is clear that this is analogous to distillation in the liquid state. The temperature at which the vapour pressure of a solid becomes equal to the external pressure is called the "sublimation point". Substances which sublime on heating cannot be melted unless an increased pressure is put upon them. If this is done, the vapour pressure has to reach a much higher value before the substance can "boil" away, and before this happens the melting point may be reached.

When a solid is sublimed, heat is absorbed analogous to latent heat of evaporation of a liquid. This is called the heat of volatilisation, and, at the sublimation point, it is equal to the sum of the latent heat of fusion and of evaporation.

SUGGESTIONS FOR FURTHER READING

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CHAPTER IX

LIQUIDS

SECTION 1.—LIQUEFACTION OF GASES

159. Critical Phenomena.—All gases can be liquefied if subjected to decrease in temperature and increase in pressure. The effect of temperature is rather more important than that of pressure, for whilst it is possible to liquefy all gases at atmospheric pressure, it is quite impossible to liquefy many of the known gases at atmospheric temperature. It was first found by Cagniard de la Tour, when experimenting with ether, that there is a temperature above which it is impossible to liquefy ether vapour, no matter what pressure is applied, but it was not until the work of Andrews on carbon dioxide that any significance was attached to this important observation. The temperature above which it is impossible to liquefy a gas, no matter what pressure is applied, is called the *critical temperature*. At this temperature, a certain pressure will have to be used to cause liquefaction, and this is called the *critical pressure*. The volume occupied by a certain mass of the gas at the critical temperature and pressure is called the *critical volume*, and is usually expressed as the volume in litres occupied by one gram-molecule of the gas at this temperature and pressure, though it is sometimes given as the ratio of the volume that the gas has at the critical temperature and pressure, to that which it would have at 0°C. and 760 mm. It is this value that is given in Table XXXVIII.

160. Andrews' Experiments with Carbon Dioxide.—In 1861 Andrews carried out his experiments on the effect of temperature and pressure on the volume of carbon dioxide. The apparatus used consisted of a sort of hydraulic press, and is shown in Fig. 99. The tube A was a capillary tube, and contained the gas. It was closed by a mercury seal, held in position by capillary forces. This tube was placed in a copper vessel filled with water, and provided with a screw C at the bottom. An

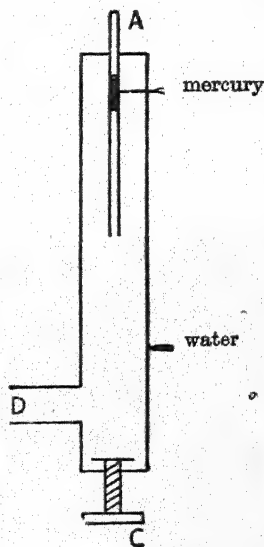


FIG. 99.—Andrews' Apparatus.

exactly similar tube with air in the capillary was joined at D, and served as a manometer. Pressure was applied to the gas by screwing up the screw C, and in this way a pressure of 400 atmospheres was obtained. The upper part of the carbon dioxide tube was surrounded by a heating bath, so that its temperature could be varied. It was found that above 31.1°C . no liquefaction would take place, no matter what pressure was applied to the gas.

The results of Andrews' experiments are given in graphical form in Fig. 100. The pressure is plotted against the volume, the curves thus

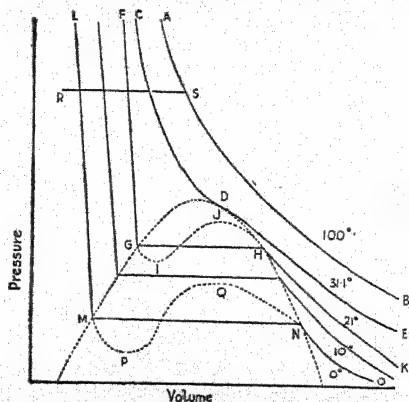


FIG 100.—Isotherms for Carbon Dioxide.

obtained being called isotherms, as each curve applies, of course, to one particular temperature only. If the equation

$$pv = k$$

is plotted in this way, the curve obtained is a rectangular hyperbola, and this should be the curve obtained with a perfect gas. It is quite clear that carbon dioxide does not give a rectangular hyperbola, although, with increasing temperature, the curve approximates to one. The temperatures are marked on the various isotherms.

The isotherm AB shows the way in which p varies with v at 100°C . This is nearly a rectangular hyperbola, but deviates from the correct form slightly. The 31.1°C . isotherm has a marked deviation from the perfect form, and shows a slight bump at D. Below this temperature, the isotherms break up into three parts. Consider the isotherm for 21°C ., FGHK. The part KH represents the effect of pressure on the volume of the gas. At H, liquid begins to appear, and the effect of the great volume change when this occurs makes itself apparent by the horizontal part of the curve, GH. When all the gas has liquefied, increase in pressure causes only a slight change in volume of the liquid, because liquids are so difficult to compress. This is represented by the portion

of the curve GF, which is almost vertical. It is sometimes possible to take the gas a part of the way over the dotted lines, HJIG, but this represents a metastable condition, and is difficult to realise. The isotherms below this temperature are all of the same form, as is shown by that for 0°C .

The isotherm, CDE, is the last one for which liquefaction occurs, and therefore indicates the critical temperature and pressure. In this isotherm the horizontal portion has become reduced just to zero.

All gases have similar isotherms to those of carbon dioxide, although the critical temperatures vary greatly. It has been found that the ends of the horizontal portions of the isotherms, when joined, form a parabola, and the apex of this is, of course, on the critical isotherm.

161. The Determination of the Critical Constants.—The *critical temperature* is fairly easily found by sealing up some of the liquid gas in a strong glass tube and gradually warming it in a suitable bath. In the case of sulphur dioxide, or carbon dioxide, a gently heated water bath is suitable. The temperature at which the boundary between gas and liquid disappears is the critical temperature.

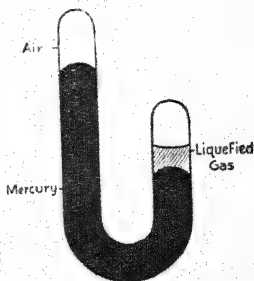


FIG. 101.—Determination of Critical Pressure.

The *critical pressure* can be obtained by using the apparatus shown in the diagram. A quantity of the liquid and vapour is enclosed in one limb of the tube, and is separated from air in the other limb by a column of mercury. The limb containing the liquefied gas is gradually heated, as in the determination of critical temperature, until the boundary between liquid and gas disappears. The volume of the air in the opposite limb is then noted; from this the critical pressure can be calculated.

The *critical volume* is rather more difficult to determine, but can be obtained from the rule of Cailletet and Mathias. The rule states that the mean values of densities of liquid and saturated vapour for any stable substance are a linear function of the temperature. Thus, if the density of a liquid is plotted against temperature, a curve BC (Fig. 102) is obtained. If the density of the saturated vapour is plotted in a similar way, the curve AC is obtained. The two curves must meet at C, corresponding to the critical temperature; for, at this point, liquid and vapour become co-existent and identical, and the point C must give the critical density. It is the point at which the

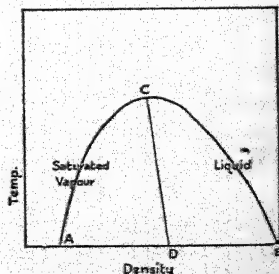


FIG. 102.

line CD intersects ACB, CD being the straight line obtained by joining the mean values of the density of the vapour and the liquid at a number of different temperatures, as stated by the rule of Cailletet and Mathias. The critical volume is readily obtained from critical density.

Some values of the critical constants for common gases are given in the accompanying table.

TABLE XXXVIII.—CRITICAL CONSTANTS.

Gas.	Critical Temp. °C.	Critical Press. Atm.	Critical Volume.
Hydrogen . . .	- 234.5°	20	0.00264
Oxygen . . .	- 118°	50	0.00426
Nitrogen . . .	- 146°	33	0.00517
Carbon dioxide . .	31.1°	73	0.0066
Carbon monoxide . .	- 141.1°	35.9	0.00505
Air . . .	- 140°	39	0.00468
Water . . .	374°	218.5	0.00386

162. Continuity of State.—If the experiment on the determination of the critical temperature or pressure of a gas has been carried out, it will have been noticed that at the critical temperature the boundary of the liquid disappears. At this temperature, the liquid and the gas phases become identical. This is due to the reduction of the surface tension of the liquid to zero. The surface tension of a liquid decreases with temperature, so as the temperature of a liquefied gas is raised, the meniscus becomes flatter and flatter. Now, the surface tension measures the work that has to be done by the surface to increase its area. If the surface tension becomes very small, very little work will have to be done to increase its surface area. So, near the critical point, the surface becomes unsteady, and ultimately disappears entirely, when the critical point is reached.

If it is possible then to pass from gas to liquid, and *vice versa*, without any abrupt change in state. Thus, take liquid carbon dioxide under conditions represented by the point R in Fig. 100. On heating this carbon dioxide, we can suppose that its condition at any given temperature is represented by some point on the line RS, if its pressure is kept constant. Suppose it is heated to 100° C., then S will be on the 100° C. isotherm. Somewhere along the line RS the carbon dioxide will have become gaseous, though the change will not have been abrupt. The pressure may now be decreased, when the carbon dioxide, now

gaseous, follows the isotherm AB. It is actually impossible to detect at what point the liquid becomes gas.

This phenomenon is termed "continuity of state".

163. Van der Waals' Equation and the Critical Phenomena.—Remarkable confirmation of the general validity of van der Waals' equation is furnished by its application to critical phenomena. As already mentioned, the isotherms obtained by plotting the curve

$$pv = k$$

are rectangular hyperbolæ. If we substitute van der Waals' equation for Boyle's Law, we have

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad . \quad . \quad . \quad (1)$$

Rearranging this in descending powers of v , we have

$$pv^3 - (RT + pb)v^2 + av - ab = 0$$

which is a cubic equation in v .

When plotted, the isotherms obtained are shown in Fig. 103, which gives the actual theoretical isotherms for carbon dioxide, calculated from equation (1). a has been taken as 0.00874, and b as 0.0023. By putting p and v equal to 1 and $T = 273$, a value for R is obtained. Then, substituting the values of p from about 40–120 atmos., corresponding values of v are deduced.

It is seen that the curves resemble the experimental isotherms of Fig. 100, with the horizontal part omitted; the latter is replaced by a curved portion, ABCD, resembling the dotted parts of the isotherms.

It has already been stated that these parts of the curve represent metastable conditions, e.g., superheated liquid and supersaturated vapour. The whole course of the dotted lines, however, has never been realised experimentally.

It is possible, by choosing suitable values for p and T , to make

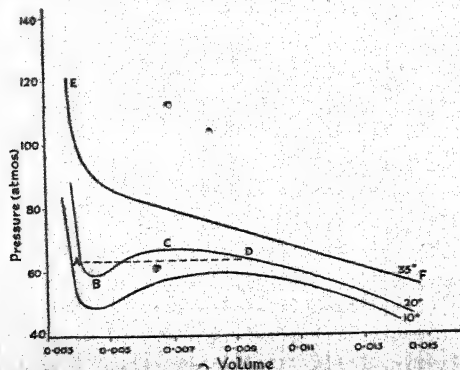


FIG. 103.—Theoretical Isotherms for CO_2 .

the cubic van der Waals' equation have equal roots. When this happens, the two humps AB and CD coincide, and a curve such as that shown at EF in Fig. 103 is produced. Comparing Fig. 103 with Fig. 100, it is seen that EF corresponds to the critical isotherm, CDE (Fig. 100). It should therefore be possible to calculate the critical constants by making use of the conditions that the equation should have equal roots.

When the three roots become identical, the root obtained, v , must be equal to the critical volume v_c .

$$\therefore v_c = v$$

and

$$(v - v_c)^3 = 0.$$

Expanding this,

$$v^3 - 3v^2v_c + 3v_c^2v - v_c^3 = 0. \quad (1)$$

Compare this with the expanded form of van der Waals' equation:—

$$pv^3 - (RT + pb)v^2 + av - ab = 0.$$

Bringing the coefficient of v^3 to unity,

$$v^3 - \left(\frac{RT + pb}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0 \quad (2)$$

When equation (2) has three equal roots, it must be identically equal to equation (1).

Equating the coefficients of v^2 in the two equations,

$$3v_c = \frac{RT + pb}{p} \quad (3)$$

Equating the coefficients of v ,

$$3v_c^2 = \frac{a}{p} \quad (4)$$

Equating the numerical terms,

$$v_c^3 = \frac{ab}{p} \quad (5)$$

From (4) and (5),

$$v_c = 3b \quad (6)$$

Since when all the roots are equal the values of v , p and T in the equation are the critical values, v_c , p_c and T_c , the values of p and T obtained from equations (3), (4), (5) and (6) will be the critical values. Thus, from (5) and (6)

$$27b^3 = \frac{ab}{p},$$

$$\therefore p = p_c = \frac{a}{27b^2} \quad (7)$$

Substituting the values previously obtained for p_c, v_c, T_c , we have

$$\left(\pi \frac{a}{27b^2} + \frac{a}{9b^2\phi^2} \right) (3b\phi - b) = \frac{8aR}{27Rb} \theta$$

or
$$\left(\pi a + \frac{3a}{\phi^2} \right) (3b\phi - b) = 8\theta ba$$

or
$$\left(\pi + \frac{3}{\phi^2} \right) (3\phi - 1) = 8\theta.$$

ϕ is called the *reduced volume*, π the *reduced pressure*, and θ the *reduced temperature*. It is seen that this is a perfectly general equation holding for all gases, since the values of the critical constants have cancelled out. Hence this equation represents, as accurately as van der Waals' equation can, the isotherms of any gas. If two substances with the same reduced pressure and the same reduced temperature are taken, they will have the same reduced volume. The accuracy of this can be judged by considering the following table. When two or more substances have the same reduced pressure and temperature they are said to be in *corresponding states*. The law of corresponding states says that when this is so, the volumes of the substances will be the same fraction of their critical volumes.

In the table below, θ for each set is approximately constant, and it is found that ϕ (liquid) is approximately constant. The agreement is not so good for ϕ (vapour).

TABLE XXXIX.—CORRESPONDING STATES¹

$$\frac{p}{p_c} = \pi = 0.08846.$$

Substance.	$\theta = \frac{T}{T_c}$	ϕ (Liquid).	ϕ (Saturated vapour).
Methyl alcohol . . .	0.7734	0.3949	34.2
Ethyl alcohol . . .	0.7794	0.4047	32.1
Propyl alcohol . . .	0.7736	0.4028	31.1
Benzene	0.7282	0.4065	28.3
Carbon tetrachloride . . .	0.7251	0.4072	27.4
Stannic chloride . . .	0.7357	0.4021	28.1
Ether	0.7380	0.4030	28.3

$$\phi (\text{liquid}) = \frac{\text{vol. of liquid}}{\text{critical vol.}}; \phi (\text{satd. vap.}) = \frac{\text{vol. of satd. vapour}}{\text{critical vol.}}.$$

¹ Data selected from values obtained by S. Young, 1892. For data for other substances see S. Young, "Stoichiometry" (Longmans, 1908), p. 219.

It has been found empirically that the boiling points of substances at atmospheric pressure are frequently about two-thirds of the critical temperature, both being measured on the absolute scale. This must not be regarded as perfectly general, but provides a certain amount of justification for comparing the properties of substances at their boiling points rather than at any other arbitrary temperature, for the boiling points are, approximately, corresponding temperatures.

TABLE XL.—BOILING POINT AND CRITICAL TEMPERATURE

Substance.	B. P. T_b . ° Abs.	Critical Temp. T_c . ° Abs.	T_b/T_c .
Sulphur dioxide . . .	263.0	430.25	0.611
Carbon dioxide . . .	194.5	304	0.640
Chlorobenzene . . .	405.0	633	0.641
Ether	307.6	466.8	0.658
Benzene	352.6	561	0.629
Water	373.0	647.3	0.577
Ammonia	234.5	404	0.580
Acetic acid	391.5	594.6	0.658

165. Liquefaction of Gases.—It is now possible to liquefy, and even solidify all the known gases.

The first reference to an attempt to liquefy a gas was that of Boerhaave, who in 1732 tried to liquefy air. We now know that this attempt was particularly ambitious, for air resisted liquefaction for a long while. Boerhaave, like many another of the early workers, succeeded only in liquefying the water vapour in the air.

In 1799, Von Märum liquefied ammonia, one of the more easily liquefied gases, at ordinary temperatures by subjecting the gas to a pressure of about three atmospheres. In the same year, de Morveau, de Fourcroy and Vauquelin liquefied ammonia by using a freezing mixture which enabled them to reach the temperature of -40°C ., at this time a record in low temperatures. About this time, too, Monge and Clouet liquefied sulphur dioxide, another of the easily liquefied gases, merely by cooling. There is no doubt that erroneous conclusions were reached in much of this early work, owing to the very imperfect drying of the gases used, the condensation of the water vapour giving the impression that the gas itself had been liquefied.

In 1805, Northmore carried out some of the most important of the early work, and succeeded in liquefying chlorine, hydrogen chloride, and

sulphur dioxide by applying pressure; but he failed with carbon dioxide, the apparatus exploding.

The work of Faraday carried out in 1823 is well known. He used a V-tube, in one limb of which the gas was prepared, whilst in the other it was liquefied under its own pressure, and with the help of external cooling. Faraday liquefied sulphur dioxide, hydrogen sulphide, carbon dioxide, nitric oxide, cyanogen and ammonia; and Davy, using the same method, liquefied hydrogen chloride.

Colladon tried to liquefy air by submitting it to high pressure and cooling. Air was confined in a thick glass tube, sealed with mercury, and so arranged that more mercury could be forced into the tube by hydraulic pressure. Although he reached a temperature of $-30^{\circ}\text{C}.$, and a pressure of 400 atmospheres, the air was not liquefied. We now know that this was because the critical temperature had not been reached, and that no matter what pressure was applied above that temperature the gas would not liquefy.

Thilorier, using a Faraday's apparatus constructed of cast iron, tried to liquefy carbon dioxide, but the vessel burst. Later, however, he was able to liquefy, and even solidify, carbon dioxide, and was the first to use a freezing mixture of solid carbon dioxide and ether, giving a temperature of $-110^{\circ}\text{C}.$, a temperature hitherto unreachd.

In all the cases described above, a gas was liquefied by the action of pressure and cooling, either together or singly. Certain gases, amongst which were hydrogen, oxygen, and nitrogen, were found to resist liquefaction under these circumstances, and they were therefore called the "permanent gases". They were not long to remain as permanent gases, however, for in 1877, Cailletet and Pictet succeeded in liquefying oxygen and hydrogen.



FIG. 104.—Faraday's Tube.

The various method for liquefying gases that were used later, depend upon the development of methods for producing intense cold. These methods may be summed up as follows:—

- (1) The use of freezing mixtures.
- (2) Cooling by the adiabatic expansion of cold compressed gases.
- (3) Cooling by the rapid evaporation of volatile liquids.
- (4) Cooling by the Joule-Thomson effect.
- (5) Cooling by adiabatic demagnetisation (de Haas).

(1) Freezing mixtures were used quite early in the history of the liquefaction of gases, as the above account shows. However, their use is very limited, for it is difficult to obtain a freezing mixture which gives a sufficiently low temperature.

(2) The method of cooling by the adiabatic expansion of a cold compressed gas was first made use of by Cailletet, who succeeded in lique-

fying air by this method. Air was expanded from high pressure, and the cooled air thus produced was used to cool incoming air. The effect was thus cumulative.

Cailletet had the idea for this method forced upon him more or less by accident, for he noticed that on reducing the pressure of some gaseous acetylene, a thick mist was produced in the gas. Thinking this was only moisture he decided to try it with pure acetylene, and then discovered that the mist was actually made up of fine drops of the liquefied gas.

Cailletet constructed an apparatus with which he could liquefy many common gases. The gas was contained in a thick glass tube over mercury, and mercury was pumped in to compress the gas. The apparatus was so designed that the pressure could be quickly relieved, so that the gas could be alternately compressed and expanded with some rapidity. In this way he liquefied acetylene and nitrous oxide, and later carbon monoxide and oxygen, which had previously been regarded as "permanent gases".

Another application of this method was made by Claude, who liquefied air. This process enjoyed considerable popularity. The apparatus is represented diagrammatically in Fig. 105.

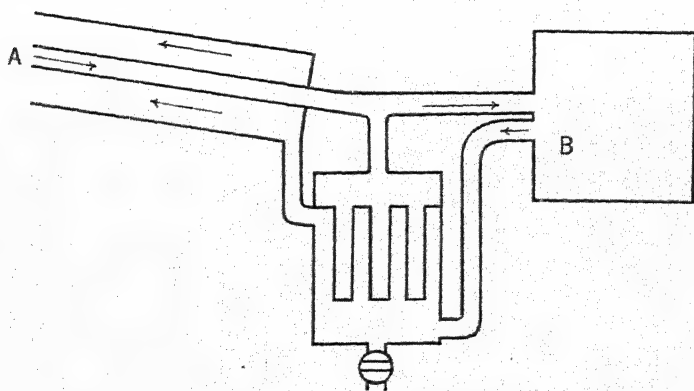


FIG. 105.—Claude's Apparatus.

The air was purified, and compressed to about 40 atmospheres and passed through the tube A into an apparatus B, in which it expanded, performing external work. The cooled and expanded air travels through the liquefier in the direction shown by the arrows, and finally passes along the outer tube of the heat exchanger A. In this way it cools the incoming gas, and this goes on until liquid air begins to collect in the liquefier.

(3) The fact that a liquid could be cooled by its own rapid evaporation was known as early as 1755, when water was frozen by rapidly

evaporating it. In 1862 the first ammonia refrigerator was made. The method depends, of course, on the taking up of the latent heat of evaporation of the substance. This heat must be supplied from somewhere, and it comes from the liquid. It was found possible by rapidly evaporating one liquefied gas to obtain a temperature low enough to liquefy another gas, and in this way the use of excessive pressures was avoided. Pictet was the first to use what is called the "cascade" method of liquefying gases. Pictet cooled a gas, B, below its critical temperature by the rapid evaporation of another gas, A, and then used the evaporation of the liquid, B, to cool another, C, and so on. In one series of experiments, sulphur dioxide was evaporated round carbon dioxide, which then liquefied fairly easily and carbon dioxide was then allowed to evaporate round a tube of oxygen. On allowing the oxygen to expand a mist was formed which Pictet thought was solid oxygen, but which was probably the liquefied gas.

In 1883, Wroblewsky and Olschewsky cooled the condensing tube of Cailliet's apparatus with ethylene evaporating under reduced pressure, and further cooled by solid carbon dioxide. A little liquid oxygen was thus obtained.

It may be noted that the critical temperatures of hydrogen and helium (31° and 5.15° Abs. respectively) are so much below the temperatures attainable by the evaporation of gases of higher boiling point that the cascade method cannot be applied.

The lowest temperatures recorded before the work of de Haas on adiabatic demagnetisation were obtained by the use of liquid helium, boiling under reduced pressure. In this way, Kamerlingh Onnes reached a temperature of 0.82° Abs., and Keesom one of 0.71° Abs.

(4) When a highly compressed gas is allowed to expand into a region of low pressure so that no work is done against external pressure, a slight cooling effect is noticed. This is called the Joule-Thomson effect. The cooling is due to the fact that internal work is done by the gas in overcoming the attractive forces between the molecules, which have already been referred to in dealing with the van der Waals' a factor (§163). This effect is to be carefully differentiated from the cooling produced when a gas expands adiabatically, for in this case the gas does external work.

The Joule-Thomson effect would not exist if a gas were perfect, for then there would be no attractive forces between the molecules. It is greater the lower is the temperature.

This effect is used in the Linde process for liquefying air. The apparatus is shown diagrammatically in Fig. 106. The air to be liquefied is first freed from impurities (carbon dioxide and water vapour), which would otherwise condense and block the apparatus. The air then enters the inner tube of the concentric pipes at A at a pressure of about 200 atmospheres. This tube is hundreds of yards long, and is coiled spirally to save space. By regulating the valve C the air is allowed

suddenly to expand in the chamber D to a pressure of about 50 atmospheres. The air, thus chilled, passes back through the tube B which surrounds the tube A. The incoming air is thus cooled even more before it expands. The air that passes first through the apparatus goes back to the pumps, where it is compressed again to 200 atmospheres and passed through the apparatus again. Finally, liquid air issues from the jet. The tubes are all surrounded with insulating material, such as wool and feathers.

Hydrogen behaves anomalously with regard to the Joule-Thomson effect. Instead of cooling when suddenly expanded, it warms up; and so it is clear that this method could not be applied to the liquefaction of this gas. When, however, the gas is cooled to about -80°C ., it behaves normally, and after this point, cools on expansion. This temperature is called the *inversion temperature*. Dewar liquefied hydrogen in 1898 by first cooling it to below the inversion temperature by means of liquid air, and then applying the ordinary Linde process.

Helium also behaves like hydrogen, but has a much lower inversion temperature (-240°C .) to which it can be reduced by cooling with liquid hydrogen. The Linde process is then applied, when the gas can be liquefied.

Helium has been solidified by Kamerlingh Onnes, who has carried out a great deal of research on the properties of substances at these very low temperatures.

Liquid air is manufactured in large quantities for the preparation of oxygen, though usually the process is continuous, the liquid air not being separated. For this purpose, the Claude method is employed for the liquefaction of air, and this apparatus is coupled to a Linde oxygen column.¹

(5) Debye (1926) and Giauque (1927) came to the conclusion that when a magnetised body is demagnetised adiabatically (*i.e.*, in such a way that heat can neither enter nor leave the system), the temperature of the body must fall. This method has been tested practically by W. J. de Haas. It can be shown that the effect is best observed at low temperatures, and by substances which are not ferromagnetic. Using cerium fluoride, cooled before the demagnetisation process by liquid helium, de Haas was able to reach a temperature of 0.27°Abs. ; later experiments, using dysprosium ethyl sulphate, gave a temperature of 0.14°Abs. ; and, in 1933, a temperature of 0.085°Abs. was attained, using cerium ethyl sulphate. de Haas believes that it will be possible by

¹ For details, see "Inorganic and Theoretical Chemistry", Sherwood Taylor (Heinemann), §678.

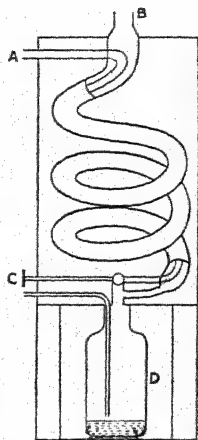


FIG. 106.—Liquefaction of Air (diagrammatic).

this method to reach the Absolute Zero, though this has not yet been accomplished (1950).

The method is mentioned here merely as one of producing intense cold. It has not been, and is not likely to be, used for the liquefaction of gases.

SUMMARY

By cooling and compressing gases, they may be liquefied. There is, however, a certain temperature above which a gas cannot be liquefied, no matter how great is the applied pressure; this is the *critical temperature*. The pressure which must be applied at this temperature, to cause liquefaction, is called the *critical pressure*. The volume occupied by 1 gram-molecule of the gas at the critical temperature and pressure is the *critical volume*. The values of the critical temperature, pressure, and volume may be obtained in terms of the van der Waals' constants, a and b , by expressing the condition that the van der Waals' equation may have equal roots. The observed isotherms (pressure plotted against volume) of gases agree with the theoretical curve given by the van der Waals' equation. The ratios of the pressure, volume and temperature of a gas to the critical pressure, volume and temperature respectively are called the *reduced pressure, volume and temperature*. When two or more substances have the same reduced pressure and temperature, they will have the same reduced volume (*Law of Corresponding States*).

Methods of liquefying gases depend upon the production of intense cold. This can be done (1) by the use of freezing mixtures, (2) by the adiabatic expansion of cold compressed gases, (3) by the rapid evaporation of volatile liquids, (4) by the use of the Joule-Thomson effect, (5) by adiabatic demagnetisation.

SECTION 2.—PROPERTIES OF LIQUIDS

A. VAPOUR PRESSURE

166. Definitions.—Every solid and every liquid possesses a vapour pressure which is a measure of the tendency of the substance to evaporate. Over every liquid there is a certain pressure of its vapour, the magnitude of which depends upon the temperature. Thus, if a liquid were to be sealed up in an evacuated tube, there would be molecules of the substance in the vapour state over the liquid, and they would exert a definite pressure. There is an equilibrium between the liquid and its vapour, as many molecules being lost from the surface of the liquid and then existing as vapour, as re-enter the liquid in a given time. The pressure of vapour which exists over any liquid or solid at any temperature, the equilibrium condition having been attained, is called the *vapour pressure*.

The vapour pressure of a liquid varies a great deal with temperature, and if the values of the vapour pressure are plotted against temperature, a curve of the form shown in Fig. 107 is obtained.

When the vapour pressure of a liquid is equal to the pressure applied externally, the liquid boils, and evaporates freely.

It has been found, however, that the presence of any indifferent gas reduces the pressure of vapour in equilibrium with its liquid, although this is contrary to Dalton's Law of Partial Pressures. Hence, for accurate work, the *boiling point of a liquid is defined as the highest temperature that can be reached by a liquid under a given pressure of its own vapour when heat is applied externally and evaporation occurs freely from the surface.*

At 100°C. , the vapour pressure of water is 760 mm., and hence water would boil at 100°C. when the pressure of water vapour over it is 760 mm. This will only differ a little from the temperature recorded when the total pressure is 760 mm.

When the vapour is in equilibrium with its liquid, it is said to be saturated vapour. When the pressure is less than this value, the vapour is said to be unsaturated.

167. Determination of Vapour Pressure.

—This can be carried out by two general methods: (1) the static method, by which the substance is caused to evaporate in a Torricellian vacuum, and the depression of the mercury column is noted; and (2) the dynamic method, in which the liquid is made to boil under a definite pressure, and the temperature of the vapour is noted.

As an example of the first of these methods, two barometer tubes may be taken, filled with mercury, and inverted over mercury in order to form two barometers. One of these is kept for reference purposes, whilst about 1 c.c. of alcohol, or some other liquid is passed up the other by means of a bent pipette. After waiting a moment or two, the difference in height of the two barometers is measured, best by means of a cathetometer. This difference is due to the vapour pressure of the substance. There will also be a slight depression of the mercury due to the weight of the liquid added, but this may be neglected. The apparatus can be modified to give the vapour pressure at any given temperature by surrounding it with a heating jacket.

Smith and Menzies devised a convenient static method for the direct measurement of vapour pressures. This instrument, called the isoteniscope is shown in Fig. 108. The liquid under investigation is introduced into the apparatus so that the small bulb A is about half full and the liquid stands about half-way up the limbs of the U-tube B. The apparatus is immersed in a constant temperature bath, and a pressure gauge and large regulator bottle are connected at C (this part of the apparatus is similar to that shown in Fig. 109). After any air

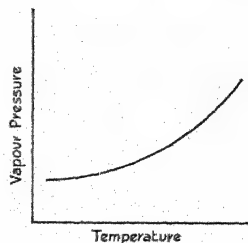


FIG. 107.—General Form of Vapour Pressure-Temperature Curve.

present has been boiled out, the pressure is reduced until the liquid in A begins to boil. The pressure in the regulator attached to C is adjusted until the level of liquid is the same in both limbs of B. The pressure registered by the manometer is the vapour pressure of the liquid at the temperature of the bath.

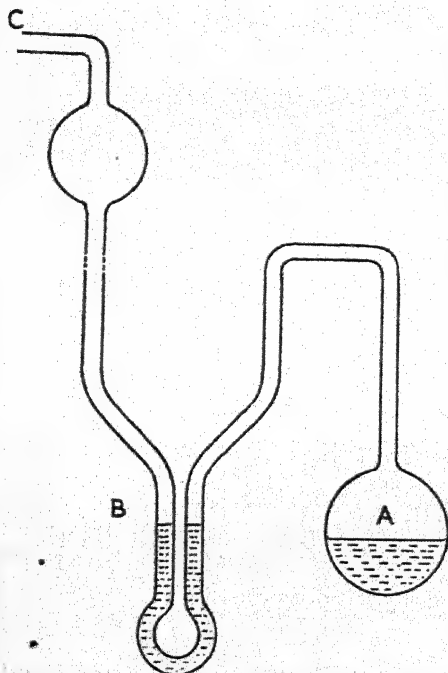


FIG. 108.—Smith and Menzies Isoteniscope.

The method of Ramsay and Young gives results of a high degree of accuracy. The apparatus is shown in Fig. 109. A boiling tube, with fairly strong walls and provided with a side-tube, should be chosen for A. The rubber stopper closing this tube is provided with a tap-funnel, and a thermometer, the bulb of which is surrounded with cotton-wool tied on with thread. This should not be too thickly covered. The stem of the tap-funnel is bent so that it just touches the cotton-wool. The pressure gauge, B, consists of a long tube dipping into mercury. C is a large bottle—a Winchester bottle answers the purpose quite well — and serves to minimise the effect of leaks. D is a tube

attached to a capillary, by means of which air can be slowly passed into the apparatus. The tube A is placed in a water-bath.

The first step is to test the apparatus to see that there are no leaks, and this is best done by evacuating by means of the filter-pump until a pressure of about 25 mm. is reached. When the pump is turned off, and the tap closed, there should be no alteration in this pressure after ten minutes. Having made sure that there are no leaks, a drop of the substance of which the vapour pressure is required is allowed to drop through the tap-funnel. The water-bath is now heated to about $50^{\circ}\text{C}.$, as indicated by a thermometer (not shown in Fig. 109). The temperature indicated by the thermometer in A will be less than that of the bath, and after a little while it will become steady when the vapour pressure of the liquid is equal to the pressure in the apparatus. Suppose that the temperature at the start is greater than this value. Then some of the

liquid will evaporate and thus cool the thermometer. If the temperature is too low, some of the vapour will condense on the thermometer and warm it up. The steady temperature reached, and the height of the mercury in the pressure gauge, are read. When the latter reading is subtracted from atmospheric pressure, the vapour pressure of the liquid at the temperature indicated by the thermometer in A is given.

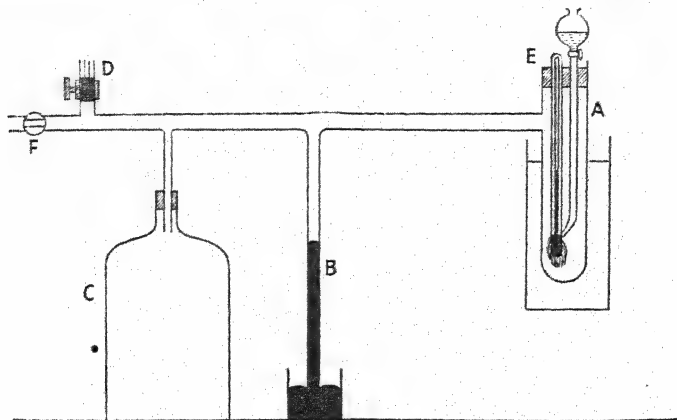


FIG. 109.—Ramsay and Young's Apparatus.

By admitting air into the apparatus through D, further readings may be obtained at higher temperatures. For this, of course, the temperature of the heating bath will have to be raised a little.

Another method of determining the boiling point at different pressures, for that is all that has been done in the above experiment, has been devised by Smith and Menzies. The same apparatus for producing the reduced pressure is used (Fig. 109). A bulb-tube of the shape shown in Fig. 110 is blown, and is partly filled with the liquid under examination. It is attached to the thermometer by means of thread, and the tube is covered with high boiling paraffin placed in the boiling tube. The water-bath is heated to, say, 30°C . (it must be understood that this temperature will vary with the liquid used, and should be the lowest at which results of reasonable accuracy can be obtained), and the apparatus is evacuated. At first air bubbles, and later bubbles of vapour come from the bulb-tube, for the liquid is boiling under the reduced pressure. Now the pump is turned off by closing the tap F, and air is allowed to enter very slowly through D, until bubbles just cease to come from the tube. This means that the liquid is just on the point of boiling at the pressure and temperature indicated by the pressure gauge and thermometer respectively. The temperature of the heating bath is gradually raised, so that readings of the vapour pressure may be obtained at various temperatures. For accurate results, a correction

should be applied for the pressure of the column of oil above the bulb tube. The density of the oil must be determined to make this correction.

Another method, that will be referred to again later in connection with the vapour pressure of solutions (§ 281), consists in passing a known volume of air over the surface of the liquid, and then determining the amount of vapour that has been removed, by weighing the liquid before and after the experiment.

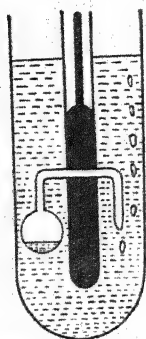


FIG. 110.—Smith and Menzies' Apparatus.

168. The Effect of Pressure on the Boiling Point of a Liquid.—It is obvious from what has been said that increase of external pressure will cause a rise in boiling point of a liquid. When specifying the boiling point of a liquid, it is, strictly speaking, necessary to mention the pressure. Thus, water boils at 100° C. only when it is in the presence of a pressure of its own vapour equal to 760 mm. of mercury. Below this pressure the boiling point will be lower; above it, it will be higher. Water can be superheated only when the pressure is increased.

The quantitative dependence of boiling point upon pressure can be obtained by the use of the Clapeyron-Clausius equation, which may be stated as

$$\frac{dP}{dT} = \frac{L}{T(v - v_1)}$$

where L is the molecular latent heat, v_1 and v are the volumes of 1 gm. mol. of liquid and vapour respectively at the boiling point T . This equation has been proved already (§ 111). It is thus seen that the rate of change of vapour pressure with temperature (dP/dT) is dependent upon the latent heat, and by a slight modification of the equation, the one may be calculated from the other.

The volume of the liquid which can be obtained by condensing a given volume of vapour is usually quite small, and can be neglected, so that the equation may be simplified to

$$\frac{dP}{dT} = \frac{L}{Tv}$$

If it can be assumed that the vapour obeys the gas laws (this is, of course, only an approximation), we have

$$Pv = RT$$

or

$$v = \frac{RT}{P} \quad \therefore \quad \frac{dP}{dT} = \frac{LP}{RT^2} \quad (1)$$

From this equation we can calculate the latent heat if we know dP/dT .

The best way of doing this is to proceed as follows. We know that

$$\frac{d \log_e P}{dT} = \frac{1}{P} \cdot \frac{dP}{dT}$$

Hence, the above equation may be written

$$\frac{L}{RT^2} = \frac{d \log_e P}{dT},$$

from which

$$L = RT^2 \frac{d \log_e P}{dT} \quad (2)$$

If $\log_e P$ is plotted against T , the curve obtained is almost a straight line, of which the slope is $d \log_e P/dT$, and can easily be found. Substituting in the equation, L can then be obtained.

Another method which does not involve plotting can be used. If L does not vary much with temperature, we can integrate equation (1) above, obtaining

$$L = \left[R \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] \cdot \log_e \frac{P_1}{P_2} = R \cdot \frac{T_1 T_2}{T_2 - T_1} \cdot \log_e \frac{P_1}{P_2},$$

where P_1 and P_2 are the vapour pressures at T_1 and T_2 respectively. Substituting $R = 2$ gm.-cals., and converting to common logarithms, we have

$$L = 2 \times 2.303 \frac{T_1 T_2}{T_2 - T_1} \log_{10} \frac{P_2}{P_1}$$

As an example, we may calculate the latent heat of evaporation of water over the range 90° – 100° C. The following data are given: At 90° C. the vapour pressure of water is 526 mm.; at 100° C. it is 760 mm.

$$\begin{array}{ll} T_1 = 363^\circ & P_1 = 526 \\ T_2 = 373^\circ & P_2 = 760 \end{array}$$

$$\therefore L = 2 \times 2.303 \times \frac{363 \times 373}{10} \log_{10} \frac{760}{526}$$

$$= \frac{2 \times 2.303 \times 363 \times 373 \times 0.1598}{10}$$

$$= 10,200 \text{ gm.-cals. per gm. mol.}$$

The latent heat in gram-calories per gram is thus $\frac{10,200}{18}$

$$= 566.5.$$

This is the average over the temperature range 90° – 100° C. The experimental value for the latent heat at 100° C. is 539, and at 90° C. 549 gram-calories per gram.

169. Relationship between the Boiling Points of Related Substances.

—By comparing the experimental values of the boiling points of various

where T_0 is the observed boiling point, P is the pressure at which it is measured, and c is a constant. The constant c has the value

$$\frac{1}{T} \cdot \frac{dT_0}{dP}, \text{ where } T \text{ is the normal boiling point.}$$

For pure, normal liquids, the value of c is in the neighbourhood of 0.00012, but varies a little from substance to substance, and the value employed in any given case should be derived, if possible, from some closely related substance.

A few values of the constant, c , are given in the table below.

TABLE XLI.—CRAFTS' RULE

Substance.	c	Substance.	c
Benzene . . .	0.000122	Methyl alcohol . . .	0.000100
Toluene . . .	0.000120	Ethyl alcohol . . .	0.000094
Naphthalene* . . .	0.000119	Acetic acid . . .	0.000107
Ethyl ether . . .	0.000121	Water . . .	0.000100
Ethyl acetate . . .	0.000114	Chloroform . . .	0.000119

B. MOLECULAR VOLUME

171. Definition.—*The molecular volume of any substance is the volume in cubic centimetres occupied by the molecular weight in grams.* It is obvious that it can be obtained by dividing the molecular weight of the substance by the density.

If Avogadro's Hypothesis were quite accurate, the molecular volumes of all gases would be the same, and equal to 22,414 c.c. Since it is not quite accurate, there are small deviations from this number for most gases.

The molecular volumes of solids and liquids were investigated, in the hope that a generalisation similar to Avogadro's Hypothesis might be made there. The success of this line of research was, however, very limited. With solids practically no useful results have been obtained, but with liquids there has been somewhat more success.

Dealing with the molecular volumes of solids, in a few cases this property has been found to be additive. Thus, if the molecular volumes of the halides of the alkali metals are compared, the substitution of one halogen for another is found to make the same difference in the molecular volume, and the substitution of one metal for another gives a characteristic difference in the molecular volume. This is clearly shown in Table XLII.

TABLE XLII.—MOLECULAR VOLUMES OF ALKALI HALIDES

Salt.	Molr. Vol. cc..	Pair.	Diffce.	Pair	Diffce.
NaCl	27.1	KCl		NaBr	
KCl	37.5	— NaCl	10.4	— NaCl	6.7
		KBr		KBr	
NaBr	33.8	— NaBr	10.5	— KCl	6.8
KBr	44.3				
		KI		NaI	
NaI	43.5	— NaI	10.5	— NaCl	16.4
KI	54.0			KI	
				— KCl	16.5
				NaI	
				— NaBr	9.7
				KI	
				— KBr	9.7

An interesting point in this connection has to do with water of crystallisation. This may be attached to the anion of the salt or to the cation. In the two cases the molecular volume of the water is different. In the case of blue vitriol, it is well known that of the five molecules of water of crystallisation, four are more or less easily driven off, whilst one is held much more firmly, and it has been suggested that it might be called water of constitution. It is now known that the four molecules which are easily detached, are attached to the cation, whilst the other one is attached to the anion. Cationic water has a molecular volume of 14.6 c.c., the same as that calculated for ice at absolute zero. The molecular volume of anionic water is 10.0 c.c., which is the same as that found when water combines with oxides to give acids, or bases. There is obviously a greater degree of combination in the second case.

122. Molecular Volumes of Liquids.—Kopp was the first to make an exhaustive study of molecular volumes. The first difficulty that confronted him was to decide at what temperature to measure the density. He took as his standard the boiling point of the liquid at atmospheric pressure. This was more or less an accident, but it was shown later to have been the right thing to do, for the boiling points are approximately the same fractions of the critical temperatures (§ 164). Other investigators have used other arbitrary temperatures, but whilst there are advantages associated with some, in general it may be said that the boiling point temperatures give the most regular results. Kopp's

determinations were made by finding the density at ordinary temperatures, and then calculating the density at the boiling point from observations of the coefficient of expansion. Since then, however, direct methods of determination have been devised.

As a result of his observations, Kopp propounded the law: "*the molecular volume of a liquid is equal to the sum of the atomic volumes of its constituent atoms.*"

This law is far from being exact. It is, however, approximately true. It has been found, as would be expected, that constitution plays a big part in deciding the molecular volume. It is very probable that the atoms in a molecule will exert some influence on each other, and in some way distort the size of the atoms. That this is the case is easily seen from Table XLIII., giving the molecular volumes of isomeric compounds.

TABLE XLIII.—MOLECULAR VOLUMES OF ISOMERS

Substance.	Mol. Vol. c.c.	Diffce. %	Substance.	Mol. Vol. c.c.	Diffce. %
n-Hexane	140.0	2.5	Propyl aldehyde	75.4	2.4
Diisopropyl	136.5		Acetone	77.2	
n-Heptane	162.6	0.37	Ethylene chloride	85.3	4.0
Isoheptane	162.0		Ethylidene chloride	88.9	
n-Propyl alcohol	81.2	1.9	Aniline	106.4	4.6
Isopropyl alcohol	82.8		Picoline	111.5	
Methyl propyl ether	105.1	3.2	Ethyl benzoate	174.6	2.4
Butyl alcohol	101.9		Phenyl propionic acid	170.4	
n-Butyric acid	108.2	0.6	Diethylamine	109.0	2.6
Isobutyric acid	108.9		Butylamine	106.2	

Obviously, if Kopp's Law were correct, the molecular volumes of isomers should be the same, since they are made up of the same atoms. As the table shows, there are a number of differences, the largest being found where the isomers fall into two distinct classes, involving a complete change in constitution, *e.g.*, methyl propyl ether and butyl alcohol. This, however, is not always so. The dichlorethanes, for example, give large differences.

Besides proposing the above law, Kopp made the following deductions:—

(1) Among analogous compounds, the same difference of molecular volume corresponds to the same difference in composition.

(2) By replacing two atoms of hydrogen by one atom of oxygen, the molecular volume is unchanged. This was later found to be untrue (see below).

(3) The atomic volume of carbon is twice that of hydrogen.

Kopp first found the molecular volume of the CH_2 group by considering a homologous series. Table XLIV. shows the mean values of the molecular volume of the CH_2 group obtained from many different homologous series. It will be noted that the value varies a good deal. Thus, in the series for the normal paraffins, shown in the second table, the value for CH_2 gets progressively greater as the series is ascended.

Kopp found the value 22 for CH_2 . Using the third rule mentioned

TABLE XLIV.—VALUES FOR CH_2

Series.	No. of Intervals.	Maximum and Minimum.	Mean.
Alcohols	8	19.7-22.4	21.1
Fatty acids	8	21.6-23.4	22.4
Aldehydes (aliph.)	4	19.0-22.0	20.7
Amines (aliph.)	5	20.4-20.6	20.5
Alkyl iodides	10	21.1-24.3	22.6
Paraffins	13	—	22.7
Esters	15	21.2-27.7	24.4
Olefines	5	20.3-23.1	21.8

TABLE XLV.—PARAFFINS

Paraffin.	Mol. Vol.	Difference.	Paraffin.	Mol. Vol.	Difference.
CH_4	38.5	—	C_5H_{12}	117.8	21.8
C_2H_6	56.7	18.2	C_6H_{14}	139.9	22.1
C_3H_8	74.6	17.9	C_7H_{16}	162.5	22.6
C_4H_{10}	96.0	21.4	C_8H_{18}	186.2	23.7

above, it follows that the amount due to C must be 11, and that due to H, 5.5. Then, from the second rule, O must be 11.

He soon found, however, that oxygen was a peculiar element to deal with. Its molecular volume varied with the states of its combination. Thus if the oxygen occurred in a carbonyl group it had a different value from that found when it occurred in the OH group or in an ether. The value for O in $\text{C}=\text{O}$ is 12.2, whereas, for that in OH or in ethers, it is 7.8.

The table below shows the values that have been arrived at for the different elements.

¹ The data for Tables XLIII, XLIV, and XLV. have been obtained from J. B. Cohen's "Organic Chemistry for Advanced Students", Vol. II. (Arnold).

TABLE XLVI.—MOLECULAR VOLUMES OF THE ELEMENTS

C	.	.	11.0	Br	.	27.8	O in OH or in ethers	.	7.8
H	.	.	5.5	I	.	37.5	O in >CO	.	12.2
Cl	.	.	22.8						

As an example, the molecular volume of acetone may be calculated.

Assuming its structure to be $\text{CH}_3 \cdot \overset{\text{O}}{\underset{\text{||}}{\text{C}}} \cdot \text{CH}_3$, the molecular volume is given by $2(27.5) + 11.0 + 12.2$, $(2\text{CH}_3 + \text{CO}) = 78.2$.

Now, the molecular weight of acetone is 58, and its density at the boiling point is 0.78 gm. per c.c. The molecular volume observed is,

$$\text{therefore, } \frac{58}{0.78} = 74.35.$$

173. Determination of Molecular Volume.—This involves determination of the density of a liquid at its boiling point. The old method used was to determine the density at 0°C ., and then determine the coefficient of expansion of the liquid. From this, the density at the boiling point could be calculated. It is, however, quite easy to determine the density of a liquid at its boiling point directly.

The density of the substance, say ethyl acetate, is first determined at room temperature by means of a density bottle. A small bulb, of the shape shown in the figure, is weighed empty, and is then filled with ethyl acetate by warming and allowing to cool with the open end under ethyl acetate in a dish. The bulb filled with ethyl acetate is weighed. The difference in the two weighings gives the weight of ethyl acetate taken, and since the density has been determined, the volume of the bulb can be calculated. The bulb is then suspended inside a flask containing ethyl acetate and provided with a reflux condenser. The ethyl acetate is boiled, and after a short time the liquid in the bulb reaches the boiling point. It expands, and a certain amount of the liquid flows out into the flask. When the liquid has been boiling for some minutes, the flask is allowed to cool, the liquid in the bulb contracts, and the bulb is taken out and weighed. The result gives the weight of ethyl acetate filling the bulb at the boiling point. The volume of the bulb is known, and hence the density at the boiling point can be calculated. The molecular volume is deduced by dividing the molecular

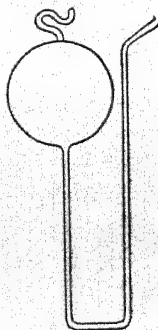


FIG. 112.—Tube for Molecular Volume Determination.

weight of the substance by its density at the boiling point. The error in this method arises from the fact that no account has been taken of the expansion of the bulb when it is heated to the boiling point of the liquid. The actual volume occupied by the liquid at the boiling point is not the volume of the bulb at room temperature, but that at the boiling point, which will be a little greater. This can be allowed for by determining the coefficient of expansion of the bulb, using a liquid of which the coefficient of expansion is known.

C. SURFACE TENSION

174. Definition.—Every liquid behaves as if it were enclosed by a skin or membrane. The surface of a liquid tends to contract, so that it must be under tension.

The *surface tension is defined as the force in dynes acting upon a line of 1 cm. length in the surface of the liquid.* Thus imagine that a cut of 1 cm. length is made in the surface membrane (the membrane, of course, does not exist, but the liquid behaves as if it does), there would be a force on each side of that line tending to open the slit, equal to the surface tension. Imagine a sheet of rubber stretched across the top of a beaker. The material is under tension. If a slit were to be made in the rubber, which was still kept under the same tension as before by some mechanical means, there would be a force on each side of the slit tending to open it.

The reason for the existence of surface tension has been mentioned when dealing with the critical phenomena (§ 127). The molecules of a liquid attract one another. A molecule in the bulk of a liquid is affected equally on all sides, but one at the boundary is only affected on one side. It is therefore acted upon by a force which tends to drag it into the interior of the liquid. That is why liquid surfaces are characterised by the fact that they tend to become as small as possible. A drop assumes a spherical shape, because this is the form that has the smallest surface area for a given volume.

It is surface tension that produces the elevation of a liquid in a capillary tube, and this phenomenon can be made use of for the measurement of surface tension.

175. Determination of Surface Tension.—There are many methods which can be used for the determination of surface tension, all of which will be found described in text-books of physics. We shall describe here, briefly, three of them—the three which are most convenient, and are the most frequently used in the physical chemistry laboratory.

(a) *The Capillary Rise Method.*—If a capillary tube is placed in a liquid it is found that the liquid usually rises in the tube. In one common case it falls, viz., mercury. Assuming that the liquid rises, suppose it reaches a height h above the level of the liquid outside.

Suppose the density of the liquid is d , and the radius of the capillary tube is r . Then the force due to surface tension is $2\pi r\gamma$, since the periphery is $2\pi r$, and the surface tension γ . This must be equal to the mass of liquid raised, $\pi r^2 h d g$. Hence,

$$2\pi r\gamma = \pi r^2 h d g,$$

$$\gamma = \frac{r h d g}{2}.$$

This is only the very elementary theoretical treatment of the problem. For the corrections due to angle of contact, text-books of physics should be consulted.

To carry out the experiment, it is seen that it is necessary to determine the radius of the tube, and the height to which the liquid rises. The density of the liquid must be known, or must be found by another experiment. The radius of the capillary is best found by placing a thread of mercury 2 or 3 cm. long inside the tube and measuring its length at different points along the tube. If the length varies, another tube should be taken, for this indicates that the bore is not uniform. When the length has been measured accurately, the mercury is removed from the tube and weighed. From the weight of the mercury, and its density, the latter being supposed known, the volume of the mercury can be obtained. The length occupied by the mercury in the tube is measured, so the area of cross-section and also the radius of the tube can be derived.

To determine the height to which the liquid rises in the tube, it is customary to use a cathetometer or travelling microscope.

From the results, the surface tension can be calculated, using the formula derived above.

(b) *The Drop-weight Method.*—The size of drop issuing from a capillary orifice is governed by the surface tension of the liquid. It was at first thought that the weight of a drop was proportional to the surface tension, but it is now known that the relationship is not so simple as this. Mathematical expressions have been derived for the relationship between the surface tension, radius of the tube, drop-weights, etc., from which the absolute value of the surface tension of a liquid can be obtained. The method is, however, more frequently used to compare surface tensions.

The instrument employed is called a stalagmometer, and consists of a bulb capillary tube, as shown in the figure. The tube is first cleaned out thoroughly with chromic acid mixture, and then with distilled water, and dried. It is then filled to the top mark with the liquid under

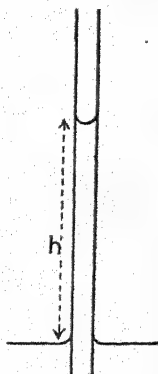


FIG. 113.—Rise of Liquid in a Capillary Tube.

observation. This is done by sucking up, as in a pipette. The tube is placed over a weighed weighing bottle, and 10 drops are allowed to fall into it. The rate at which the drops fall should be adjusted so that they come at about one every two seconds. If the liquid falls faster than

this, the drops may not be properly formed, and may be too small. The weight of the 10 drops is found. The apparatus is then carefully cleared out, and the experiment repeated with the other liquid. If m_1 and m_2 are the masses of 10 drops of the two liquids, and γ_1 and γ_2 are the surface tensions

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2}$$

If the surface tension of one liquid is known, that of the other is readily calculated. Thus, if it is required to find the surface tension of benzene, the drop-weights of water and benzene would be compared, the surface tension of water being known, having been determined by some other method.

It is sometimes easier to determine the number of drops formed by a certain volume of liquid, instead of finding the mass of a drop. In this case the stalagmometer is filled to the top mark with the liquid under test, and the liquid is allowed to flow from the apparatus until the lower mark is reached, the number of drops being counted. The purpose of the small graduated portion of the tube is to enable fractions of a drop to be judged. The same procedure is adopted with the other liquid. Suppose that one liquid, of density d_1 , produces n_1 drops, its surface tension being γ_1 , and that the other liquid of density d_2 , and surface tension γ_2 , produces n_2 drops. Then

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} = \frac{vd_1n_2}{vd_2n_1} \therefore \frac{\gamma_1}{\gamma_2} = \frac{n_2d_1}{n_1d_2}$$

FIG. 114.—
Stalagmometer.

The advantages of the drop-weight method are that it can be used at various temperatures by placing the whole apparatus in a thermostat, and that reliable results can be obtained rapidly. It suffers from the disadvantage that it is difficult to use for absolute determinations, and that the tip of the tube must be kept perfectly clean, otherwise bad results will be obtained. Care must be taken to avoid vibration during an experiment.

(c) *The Tensiometer*.—A very satisfactory determination of surface tension can be made in many cases by the tensiometric or detachment method. This method was developed by Wilhelmy and an improved apparatus is now available as a commercial instrument known as a

tensiometer. A platinum ring about 4 cm. in circumference hangs from the end of the beam of a torsion balance. The ring is dipped under the surface of the liquid and the force required to raise the ring from the surface is measured. This method can be used when only small amounts of liquid are available.

176. Variation of Surface Tension with Temperature.—The surface tensions of all substances vary with temperature. Usually there is a decrease as the temperature is increased. At first sight, over small temperature ranges, the relationship between surface tension and temperature appears to be linear, but when larger temperature ranges are used the graph of surface tension against temperature shows a curvature.

Van der Waals put forward an equation expressing the relationship, which has been modified by Sugden to the form

$$\gamma = \gamma_0 (1 - T_r)^{\frac{2}{3}} \quad (1)$$

where T_r is the reduced temperature (§ 98), and γ_0 is the surface tension of the supercooled liquid at absolute zero. γ is the surface tension at the reduced temperature T_r .

This equation is found to hold with some accuracy for most normal liquids, but there are deviations for liquids which are known to be associated, e.g., the alcohols.

177. MacLeod's Equation.—There is a relationship between surface tension and density which has been found extremely useful, as it forms the basis of the parachor (see next section). The equation was discovered by MacLeod in 1923, and states that

$$\gamma = C (D - d)^4 \quad (1)$$

where γ is the surface tension, D is the density of the liquid, and d the density of the vapour, measured at the same temperature. The constant C is found to be independent of temperature, and the equation holds with accuracy over a large temperature range for normal liquids.

Reverting now to the effect of temperature on surface tension, Ramsay and Shields found that if the quantity $\gamma \left[\frac{M}{D} \right]^{\frac{2}{3}}$, where M is the molecular weight, was plotted against temperature a straight line was obtained. What is the significance of $\gamma \left[\frac{M}{D} \right]^{\frac{2}{3}}$? The molecular volume is $\left[\frac{M}{D} \right]$, and hence $\left[\frac{M}{D} \right]^{\frac{2}{3}}$ may represent the molecular surface. The surface tension measures the surface energy, and hence $\gamma \left[\frac{M}{D} \right]^{\frac{2}{3}}$ is the molecular surface energy. The straight line referred to above does not pass through the origin, but the equation of the line is

$$\gamma \left[\frac{M}{D} \right]^{\frac{2}{3}} = k(T_c - t - 6)$$

where T_c is the critical temperature, and t is the temperature of observation. This equation is referred to as the equation of Ramsay and Shields.

Some time previous to the derivation of this expression, Eotvos had put forward the equation $\gamma \left[\frac{M}{d} \right]^{\frac{2}{3}} = k (T_c - T)$, which is not so accurate as the Ramsay and Shields' equation.

This equation has been derived more recently by considering the effect of temperature on surface tension and on density. The equation of van der Waals and Sugden has already been mentioned (last section),

$$\gamma = \gamma_o (1 - T_r)^{\frac{3}{2}} \quad (2)$$

It has been shown by Sugden that if the surface tension, γ , is eliminated from MacLeod's equation and from the equation just given, an expression of the form

$$(D - d) = D_o (1 - T_r)^{\frac{3}{2}} \quad (3)$$

is obtained connecting density and temperature. D_o is the density of the supercooled liquid at the absolute zero.

It follows from (3) that

$$\left(\frac{M}{D - d} \right)^{\frac{2}{3}} = \left(\frac{M}{D_o} \right)^{\frac{2}{3}} \cdot \frac{1}{(1 - T_r)^{\frac{3}{2}}}$$

Combining this with (2)

$$\gamma \left(\frac{M}{D - d} \right)^{\frac{2}{3}} = \frac{\gamma_o M^{\frac{2}{3}}}{D_o^{\frac{2}{3}}} (1 - T_r) = \frac{\gamma_o}{T_c} \left(\frac{M}{D_o} \right)^{\frac{2}{3}} (T_c - T),$$

$$\text{i.e., } \gamma \left(\frac{M}{D - d} \right)^{\frac{2}{3}} = k' (T_c - T).$$

This is Katayama's form of the Eotvos equation— $\gamma \left(\frac{M}{D} \right)^{\frac{2}{3}} = k' (T_c - T)$ —the forerunner of the Ramsay and Shields' equation.

Ramsay and Shields' equation is somewhat better than the Eotvos equation, but that of Katayama is better still, especially if $T_c - 6$ is substituted for T_c , making the equation

$$\gamma \left(\frac{M}{D - d} \right)^{\frac{2}{3}} = k' (T_c - T - 6).$$

It was at first thought that the value of the constant k or k' in these equations was the same for all normal liquids, and equal to 2.12. If any liquid gave a constant differing from this it was supposed to be abnormal. Many liquids, known from other experiments to be associated, such as the alcohols and water do give constants differing widely from 2.12, but it has since been shown that some perfectly normal liquids give anomalous values for k , so that this is no criterion of abnormality. (See association of liquids, § 191.)

178. The Parachor.—It has been seen in dealing with molecular volume that the value of this property is, on the whole, additive, but that there are irregularities, even when the molecular volume is found

at the boiling points, which are corresponding temperatures. The chief reason for this is the fact that every liquid has an internal pressure, due to the existence of attractive forces between the molecules. The internal pressures of various liquids are quite different, even at corresponding temperatures, and it is therefore to be expected that there will be anomalies in the molecular volumes. If we could correct for the varying internal pressure, we should obtain a property which would be truly additive.

To a certain extent, surface tension is a measure of internal pressure, for it is governed by the attractive forces between the molecules. The reason why there is such a phenomenon as surface tension is because there is an inward force acting on the molecules at the surface (§ 174). We look to surface tension, therefore, to throw some light on the correction to be applied to molecular volumes in order to make them free from anomalies.

For this purpose, Sugden made use of MacLeod's equation connecting surface tension and density,

$$\gamma = C(D - d)^4.$$

Another way of writing this equation is

$$C^{\frac{1}{4}} = \frac{\gamma^{\frac{1}{4}}}{D - d}$$

Hence, for any liquid of molecular weight M ,

$$\left(\frac{M}{D - d}\right) \gamma^{\frac{1}{4}} = MC^{\frac{1}{4}} = [P],$$

is constant. The constant $[P]$ is called the parachor. Since d is very small compared with D , the expression becomes the molecular volume multiplied by the fourth root of the surface tension. In other words, the *parachor is a measure of the molecular volume at temperatures at which different liquids have the same surface tension.*

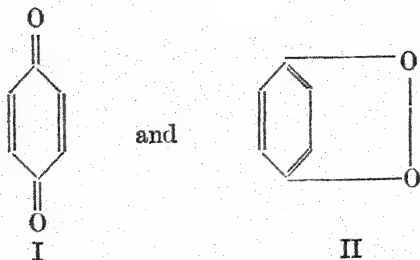
The parachor is an additive property. There are definite values associated with each atom, and also with various structures, such as the double and triple bonds, the rings, etc. The table below gives some of the values in common use:—

TABLE XLVII.—PARACHORS

H = 17.1	Triple bond	46.6
C = 4.8	Double bond	23.2
O = 20.0	3-Ring	16.7
N = 12.5	4-Ring	11.6
S = 48.5	5-Ring	8.5
Cl = 53.8	6-Ring	6.1
Br = 68.0	Single bond	0.0 (arbitrary)
I = 90.0	Semipolar double bond	- 1.6
P = 37.7	O ₂ in esters	60.0

It is obvious that, since the parachor is a strictly additive property, it cannot be used to differentiate between isomers, unless these have certain structural differences.

179. Uses of the Parachor.—In many cases the parachor has been of great use in deciding the structure of a substance. For example, two structural formulæ have been proposed for quinone,



The parachor for a substance with structure I is: $(6 \times 4.8) + (4 \times 17.1) + (2 \times 20.0) + (4 \times 23.2) + 6.1 = 236.1$.

and for a substance with structure II: $(6 \times 4.8) + (4 \times 17.1) + (2 \times 20.0) + (3 \times 23.2) + (2 \times 6.1) = 219.0$.

The values used here are taken from Table XLV. The value found by experiment is 236.8 which indicates that formula I is the correct one. The parachor has also been used to show that paraldehyde, which is made up of three molecules of acetaldehyde, has a cyclic and not a straight chain formula. The use of the parachor has helped considerably in the elucidation of many other structures, notably the structure of the isocyanide radical $^{\circ}\text{NC}$, and the constitution of the chlorides of certain dibasic organic acids, e.g., phthalyl chloride. There are numerous other problems which have been studied by means of the parachor for details of which the reader should consult Sugden's "The Parachor and Valency".

D. VISCOSITY

180. Definition.—All liquids possess a certain resistance to flow, which is called their viscosity. It is really a frictional effect due to the passage of one layer of liquid over another, and is sometimes referred to as such.

The *coefficient of viscosity* is defined as *the force required per unit area to maintain unit difference of velocity between two parallel planes in the fluid, one centimetre apart*.

The smaller the coefficient of viscosity, the more rapidly does the liquid flow. The greater it is, the less rapidly does the liquid flow. Oils,

and liquids like glycerine, have a very high coefficient of viscosity, whilst ether and similar liquids which we are accustomed to call "very mobile", possess a low coefficient.

The coefficient of viscosity is expressed in dynes per sq. cm. The unit of viscosity is called the poise (from the name of the investigator who did most of the early work in the subject—Poiseuille).

181. Determination of Viscosity.—It can easily be shown that when a liquid flows through a capillary tube of radius r , for a time t ,

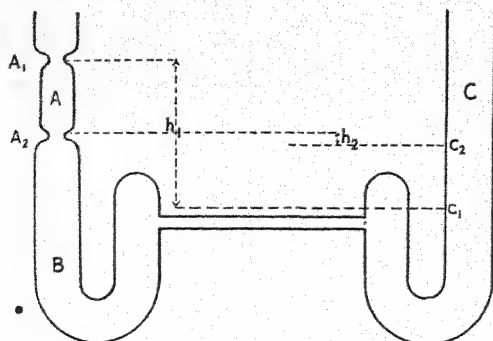


FIG. 115.—Diagram of Koch's Apparatus (after J. Newton Friend).

under a constant pressure head p , the volume of liquid v , issuing from the tube, is given by

$$v = \frac{\pi p t r^4}{8 l \eta} \quad (1)$$

where η is the coefficient of viscosity and l is the length of the tube.

For the purposes of a simple experiment, it is possible to keep the pressure head almost constant by having a large reservoir of liquid and by carrying out the experiment over not too long a time. The fall in level of the liquid in the reservoir will then not be appreciable. For this experiment, a capillary tube of known length is connected to the bottom outlet of an aspirator, and at a given instant a tap is opened and the liquid is allowed to flow through the tube. After the flow has continued for a definite time, determined by means of a stop-watch, the tap is closed, and the volume of liquid that has come through is measured. The radius of the tube is determined by measuring the length and mass of a mercury pellet placed in the tube. The tube should, of course, be selected for uniformity of bore, and the temperature must be kept quite constant throughout the experiment.

For the accurate determination of the coefficient of viscosity it is necessary to take into account the fact that the pressure head is not constant, and this can be done by an extension of the formula given above.

The apparatus used for a more accurate determination is that due to Koch, and shown in outline in Fig. 115.

The tubes A, B and C, have the same radius, r_1 , the liquid in A being allowed to fall from the mark A_1 to A_2 . During this time the liquid rises in C from C_1 to C_2 . In the diagram, h_1 and h_2 will be the initial and final pressure heads. Suppose the time taken for the liquid to fall from A_1 to A_2 is t secs.

In a small time dt secs., a volume dv of liquid will have passed through the capillary tube. If the pressure head at this moment is h ,

$$dv = \frac{\pi h g d r^4}{8 l \eta} dt,$$

where r is the radius of the capillary and d the density of the liquid. But, in the experiment

$$dv = -\pi r_1^2 \frac{dh}{2}, \quad \therefore v = \pi r_1^2 \frac{h_1 - h_2}{2}$$

If we substitute this value for dv in the above equation we have:—

$$-\frac{\pi r_1^2}{2} dh = \frac{\pi h g d r^4}{8 l \eta} dt.$$

Integrating,

$$-\frac{\pi r_1^2}{2} [\log_e h]_{h_1}^{h_2} = \frac{\pi g d r^4}{8 l \eta} [t]_0^t,$$

$$\therefore \frac{r_1^2}{2} \log_e \frac{h_1}{h_2} = \frac{g d r^4 t}{8 l \eta},$$

$$\eta = \frac{2 g d r^4 t}{8 l r_1^2 \log_e \frac{h_1}{h_2}};$$

but

$$v = \pi r_1^2 \frac{h_1 - h_2}{2},$$

$$\therefore \eta = \frac{\pi (h_1 - h_2) g d r^4 t}{8 l v \log_e \frac{h_1}{h_2}}.$$

As already stated, it is a difficult matter to determine the absolute coefficient of viscosity for a liquid, and, indeed, it is not usually necessary. As with surface tension, the relative viscosity of a liquid with respect, say, to water, may be determined; and then, knowing the coefficient of viscosity of water, which has been found by another experiment, the coefficient for the other liquid may readily be found.

The simplest way to do this is to make use of the Ostwald viscometer. This consists of a tube of the form shown in Fig. 116. The wider limb of the tube is first filled with the liquid under examination, say water, and it is then sucked up to a level C in the narrow limb. The water is

then allowed to flow back, and the time taken for the level to fall from A to B is noted. The liquid passes through the capillary tube BD, and it is clear from equation (1) above, that the time of flow, t , will be proportional to the coefficient of viscosity. It is also inversely proportional to the density d .

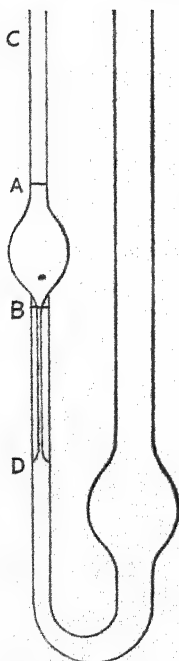


FIG. 116 — The Ostwald Viscometer.

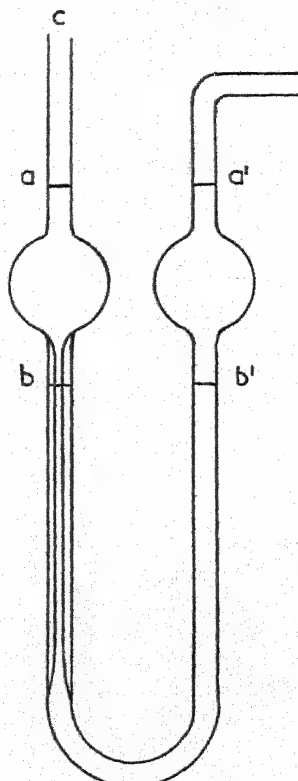


FIG. 117.—Ubbelohde Viscometer.

Hence,

$$\eta = kdt.$$

For a second liquid

$$\eta' = kd't'$$

Hence

$$\frac{\eta}{\eta'} = \frac{dt}{d't'}$$

If the coefficient of viscosity of water is known, the coefficient for the other liquid is readily found.

The result will not be quite accurate, since the pressure head will not be the same for the two liquids, owing to their differing densities.

With this apparatus it is quite easy to compare viscosities at different temperatures. The whole apparatus may be placed in a thermostat. Of course, it is necessary to maintain the temperature constant during an experiment.

There are a number of viscometers which are modifications of the Ostwald viscometer. In the Ubbelohde viscometer (Fig. 117) it is not necessary to determine the density of the liquid under investigation, as it was in the Ostwald apparatus. The two bulbs have the same volume and are at the same level (as nearly as possible). The liquid is sucked up to the levels *a* and *b'* and is driven through by applying a constant dry air pressure at *C*. The time taken for the liquid to flow from *b'* to *a'* is noted. If the time and pressure for one liquid, say water, are *t* and *p* and for a second liquid *t*₁ and *p*₁ then the viscosity of the latter can be found from the relationship $\eta_1 = \eta p_1 t_1 / pt$.

By taking the average of the times to flow from right to left and from left to right compensation is made for any differences in the volumes and levels of the bulbs. Fluctuations of pressure can also be corrected. to reduce the error caused by a varying head of liquid Ubbelohde used a capillary with a wider tube below.

There are many other types of viscometer depending upon such phenomena as the fall of a sphere through a liquid, or the force required to twist one plate relative to another in a liquid, but there is no need to describe them in detail here.

182. Viscosity and Constitution.—The connection between viscosity and constitution is not very marked, though a few relationships have been noted. For example, in an homologous series, the increase in viscosity per CH₂ group is roughly constant.

A useful relationship between viscosity and molecular volume was discovered by Dunstan; it may be expressed as follows:

$$\frac{d}{M} \cdot \eta \times 10^6 = 40 \text{ to } 60,$$

where *d* is the density, *M* the molecular weight and η the coefficient of viscosity of the liquid. This relationship holds only for normal liquids. For associated liquids, the number is considerably greater than this. The values for a few substances are given in the table below:—

TABLE XLVIII

Substance.		Formula.	$\frac{d}{M} \eta \times 10^6$
Normal Liquids	Benzene . . .	C ₆ H ₆	73
	Toluene . . .	C ₆ H ₅ . CH ₃	56
	Acetone . . .	CH ₃ . CO . CH ₃	43
Abnormal Liquids	Water . . .	H . OH	559
	Glycol . . .	CH ₂ OH . CH ₂ OH	2,750
	Glycerol . . .	CH ₂ OH . CHOH . CH ₂ OH	116,400

This expression has been used as a criterion of association (§ 191).

Measurements of the viscosities of solutions of polymers have been applied to the determination of the molecular weight of polymers. If the viscosity of a solution is η at concentration c , and the viscosity of pure solvent is η_0 , then the specific viscosity of a solution is defined by the relationship

$$\frac{\eta - \eta_0}{\eta_0} = \eta_{sp}$$

Although the function $\frac{\eta_{sp}}{c}$ is nearly constant with variation of concentration, it is found to vary in an approximately linear manner. The value of $\frac{\eta_{sp}}{c}$ obtained by extrapolating a plot of $\frac{\eta_{sp}}{c}$ against concentration, c , to zero concentration gives what is called the intrinsic viscosity, $[\eta]$.

Staudinger and later workers found empirically that the relation intrinsic viscosity $[\eta] = k\bar{M}^{-a}$ is valid for solutions of long chain molecules (such as polymers) in neutral solvents (such as benzene). K and a are constants for a particular series of long chain compounds, and \bar{M} is the average molecular weight of the long chain molecules. Originally Staudinger suggested a value of unity for a ; it has since been found to have values usually less than one. Theoretical considerations suggest that the value of a depends on the extent to which the long chain molecule is coiled. When the chain is coiled into a ball the value of a approaches zero; when the chain is kinked at random the value of a approaches 0.5 for very long chains. In using the Staudinger expression to determine the molecular weights of polymers it is necessary to determine the values of a and K for the series of compounds being studied. This may be done by finding the viscosities of two solutions of a substance for which the molecular weight has been determined independently, e.g., by osmotic pressure measurements. The Staudinger relationship is used extensively in polymer chemistry.

E. OPTICAL PROPERTIES

(a) OPTICAL ACTIVITY

183. Polarisation of Light.—By the term "optical activity" is understood the power possessed by certain substances to rotate the plane of polarisation of light.

Ordinary light may be supposed, for our present purpose, to be a transverse wave-motion. The oscillations which make up a train of waves are at right angles to the direction of propagation, but may take

place in any plane. Thus if a ray of light were travelling in the plane of this paper, the transverse oscillations themselves might take place in any plane, in the paper, or out of it. Some might be at right angles to the plane of the paper, others at 45° , or any other angle. All that is meant by saying that light travels in a certain direction is that the direction of travel of the waves is the same. No direction is specified for the actual oscillations.

If, by any means, light can be obtained in which the oscillations are all in one plane, the light is said to be polarised. Thus, if we have light travelling in the plane of this paper, and by some means or other we make all the oscillations of the light take place in the plane of the paper too, then we have light which is polarised in the plane of the paper. This plane polarisation may be brought about by various means. Thus, when light is reflected from certain surfaces there is always a considerable degree of polarisation. It may be noted here that it may not be possible to polarise a beam of light completely, but it may be possible to get the greater proportion of oscillations to take place in one plane. When light passes through certain crystals in a certain direction, it may emerge polarised. One of the best crystals for this purpose is calcite, which has the property of double refraction. When light falls on to a calcite crystal, it is split up by the crystal into two rays, the crystal appearing to possess different refractive indices for the two rays. The first is called the ordinary ray, the second, the extraordinary ray. Now, on examination, both these rays are found to be polarised, one in a plane at right angles to the other. If a crystal of calcite is so cut that only one of the rays emerges, the other being returned by internal reflection, a beam of polarised light is produced. A calcite crystal cut in this manner is called a Nicol prism.

If the beam of light emerging from a Nicol prism is passed on to another similar prism, it will get through if the second prism is in exactly the same position as the first, but if turned so that it is at 90° to the first, no light will get through, but it will all be totally internally reflected.

An illustration from Stewart's "Stereochemistry" will make this quite clear. Suppose we have two books lying on a table. A flat ruler may be made to pass through both of them. If, however, one book is placed so that its plane is at right angles to that of the other, the ruler which gets through one will not be able to get through the other. The first book stands for the first Nicol prism. Light emerging from it will be polarised in one plane—this is represented by the ruler. If this polarised light falls on another Nicol prism it may get through or it may not, it depends upon the relationship of the second prism to the first. If its crystal planes are in the same planes as those of the first the light will get through, just as when the leaves of the second book are in the same planes as those of the first, the ruler gets through. If they are at

right angles then no light gets through. The illustration fails, of course, in that a slight variation of angle between the two books means the cutting off of all possibility of the ruler from getting through, whereas in the case of light, total darkness is only attained when the two crystals are exactly at right angles to each other.

Now, certain liquids and solids are capable of rotating the plane of polarisation of light. If such a liquid is interposed between two parallel Nicols, it is found that the one no longer has to be turned through a complete right angle to get total darkness, but that they have to be at some other angle to each other. This is because, during its passage through the liquid, the polarised light has been turned through a certain angle. The rotation is progressive, and hence will depend upon the length of the substance through which the light has to pass. It is possible to turn the plane of polarisation through several revolutions if the length of substance is great enough.

Certain liquids rotate the plane of polarisation of light to the right, and are called dextro-rotatory. Others rotate it to the left, and are called laevo-rotatory. It should be mentioned that this property is not confined to pure liquids and solids, but also applies to solutions.

The amount of rotation is easily measured by means of an instrument called a polarimeter, which makes use of the facts explained above. It consists essentially of two Nicols, which can be rotated with respect to each other, i.e., one is fixed, and the other can be rotated. Between the two Nicols there is a space into which can be fitted a tube containing the liquid under examination. These tubes are made of definite lengths, 5 cm., 10 cm., 20 cm. and 25 cm., so that the length of liquid through which the light passes is known. For a complete description of the instrument the practical text-books should be consulted.

The apparatus is set up without the tube of liquid, and a beam of monochromatic light is passed through the instrument. This may be sodium light, or one of the mercury lines may be used. The light passes through the polarising prism, called the polariser, and falls on the second prism called the analyser. The analyser is turned until there is complete darkness, and the reading of the scale is taken. Now the tube of liquid is inserted. On looking through the analyser, the field now appears bright, because the liquid has rotated the plane of polarisation, and the analyser is now no longer at right angles to the vibrations of the beam. It has to be turned through a certain angle for complete darkness again to be reached. This is the angle through which the plane of polarisation has been rotated. Modern polarimeters have numerous improvements over the simple type, the essentials of which are described above.

Besides depending upon the length of the substance through which the light has to pass, the rotation α , depends upon the density of the substance, the temperature, and the wavelength of light used.

The specific rotatory power of a pure liquid is given by the equation

$$[\alpha]_D^t = \frac{\alpha}{ld}$$

where $[\alpha]_D^t$ is the specific rotatory power at a temperature t , and for light of the sodium D line, l is the length of the column of liquid in decimetres, and d is the density in grams per c.c.

For a solution, the concentration is substituted for density and the equation becomes

$$[\alpha]_D^t = \frac{\alpha}{lc}$$

The concentration c is expressed in grams per c.c. of solution.

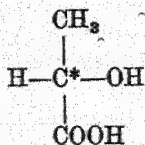
The molecular rotation is given by

$$[M]_D^t = \frac{M[\alpha]}{100}$$

where M is the molecular weight.

184. Optical Activity and Chemical Constitution.—Optical activity is bound up with asymmetry of the molecule or crystal structure. Thus, if an organic compound has an "asymmetric" carbon atom, it is optically active, and exists in two distinct forms, or more. One form is dextro-rotatory, the other lævo-rotatory to the same extent. A third form, consisting of a mixture of the other two in equimolecular proportions also exists, which can be separated by various means into the two optically active components. Such a substance is said to be "externally compensated". Sometimes, a fourth form is known, which, although optically inactive, is not a mixture of the optically active forms because it cannot be resolved into those forms by any method. This form is called "internally compensated", and exists where there are two or more asymmetric atoms in the molecule. An example of this is given by tartaric acid.

By an asymmetric carbon atom we mean one that is joined to four different atoms or groups. Thus, the compound



known as lactic acid, has an asymmetric carbon atom, indicated by the asterisk. It exists in three forms, two optically active, and a third "racemic" or externally compensated mixture.

For further details of this important subject a text-book on organic chemistry should be consulted.

As mentioned above there is a type of optical activity not dependent upon the molecule, but upon the arrangement of molecules in a crystal. The effect is best shown by quartz.

(b) MAGNETIC ROTATION

185. Methods of Observation.—If a beam of polarised light is passed through a transparent substance placed in the field of an electromagnet, so that the light travels in the direction of the lines of force, the plane of polarisation is rotated. This must not be confused with ordinary optical activity. It is a general effect, and is shown by all transparent substances, not only those having an asymmetric carbon atom. This magnetic rotation will be dependent upon the direction of the lines of force, so that by means of a suitable apparatus it is possible to reflect the light back upon itself, and thus increase the rotation. The angle of rotation, ω , is proportional to the length, l , of substance used, and also to the strength of the magnetic field, H . Hence

$$\omega = \phi l H.$$

The constant ϕ is called Verdet's constant. It has been found that this varies with the nature of the substance, the wavelength of light used and the temperature, though the influence of temperature on magnetic rotation is small.

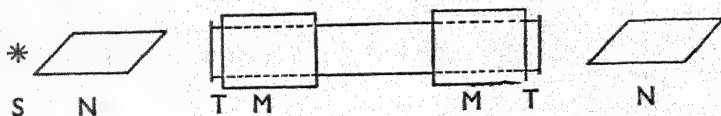


FIG. 118.—Magnetic Rotation. S = source of light, N, N = nicol prisms, M, M = poles of electromagnet, T, T = tube containing substance.

The application of magnetic rotation to the study of the structure of organic compounds was first carried out by W. H. Perkin. The method of determining magnetic rotation is a comparative one, so that it is not necessary to work with absolute units. Water is taken as the standard substance. If the same apparatus is used every time a determination is made, there is no need to introduce the length of the tube, the temperature, or the wavelength of the light used. To compare the effect of equal masses of different liquids, it is only necessary to divide the observed rotation by the density. The rotation in unit length of tube, α , divided by the density d , is called the relative specific magnetic rotation,

$$r = \frac{\alpha}{d}$$

The relative molecular magnetic rotation is given by

$$r_M = \frac{M\alpha}{m\bar{d}} = \frac{M\alpha}{18\bar{d}},$$

where M is the molecular weight of the substance, and m is the molecular weight of water.

The absolute molecular magnetic rotation, R_M , can readily be found by multiplying the right-hand side of the equation by the absolute value for water, which has been found by Rodger and Watson to be 0.01312 minutes of arc at 20° C.

$$R_M = \frac{0.01312 M\alpha}{18\bar{d}} \text{ minutes of arc.}$$

186. Magnetic Rotation and Structure.—Since isomeric substances give different values for the molecular magnetic rotation it is clear that the property is not merely additive but is also constitutive. It is impossible to give a detailed list of the results obtained here; all that can be done is to mention briefly some of them.¹

It has been found that geometrical isomers have a different magnetic rotation, the "trans" modification possessing the greater, as a rule. Optical isomers also differ in magnetic rotation, but only slightly. Thus,

Ethyl maleate	9.625
Ethyl fumarate	10.112
Ethyl tartrate	8.766
Ethyl racemate	8.759
Glucose	6.723
Galactose	6.887

From the consideration of a large number of observations on different homologous series, Perkin arrived at the value 1.023 for the CH_2 group. A list of values for the different groups has been drawn up, but it is necessary to add a "series constant", which varies with the series to which the substance belongs, when computing the magnetic rotation of a compound. Thus, the series constant for the fatty acids is 0.393, for the normal paraffins it is 0.508, and for ketones 0.375.

The method has been useful in deciding structures, *e.g.*, in cases of keto-enol tautomerism (acetoacetic ester), and was applied by Perkin to the study of the terpenes.

(c) REFRACTIVITY

187. Formulæ for Refractivity.—As a result of work begun in 1858,

¹ For a detailed account, and list of values, see Cohen, "Organic Chemistry," Vol. II. (Arnold), pp. 45-56.

Gladstone and Dale proposed that, when comparing the refractive indices of substances, the density should be eliminated, as the refractive index is largely influenced by this. They therefore used the formula

$$r = \frac{n - 1}{d}.$$

r is called the specific refractive index, or the specific refractivity; n is the refractive index, and d the density.

In 1880, a second formula was put forward simultaneously by H. A. Lorentz, of Leyden, and L. Lorenz, of Copenhagen. This was

$$r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}.$$

This formula is independent of pressure and temperature, whilst that of Gladstone and Dale is not. It is now the usually accepted formula, although that of Gladstone and Dale is still sometimes used. Whilst the latter is simply empirical, the Lorentz and Lorenz equation was derived from considerations of the Clerk Maxwell electromagnetic theory of light.

The molecular refractivity (M) is obtained by multiplying the specific refractivity by the molecular weight (m) of the substance:—

$$M = \frac{n - 1}{d} \cdot m \text{ or } M = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{m}{d},$$

Refractive index is usually determined by the refractometer. Pulfrich's refractometer is the one most frequently used. There is no space for a description of the instrument here; the practical text-books should be consulted. With a good instrument the refractive index can be determined to the fourth decimal place, so that the determination of refractivities is a matter of great accuracy. The value, of course, varies with the wavelength of the light employed, which must always be specified.

188. Refractivity and Constitution.—Refractivity is additive, and also constitutive. It has been found that similarly constituted isomers have the same refractivities; *e.g.*, the figures for isopropyl alcohol and propyl alcohol are 17.44 and 17.42 respectively (using light of the hydrogen α line, H_{α}). The values for butyl iodide and isobutyl iodide are exactly the same, 33.25. It seems reasonable, then, to assume that spatial differences do not make a great effect on the refractivity. However, differences have been found among geometrical isomers, but not among optical isomers.

By studying the refractivities of a number of homologous series, the value for CH_2 was found to be 4.57. Table XLIX. gives the values obtained for some elements and groupings.

TABLE XLIX

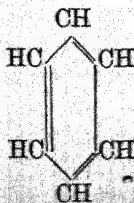
		H _a
Carbon	C	2.414
Hydrogen	H	1.092
Oxygen	O' (enol)	1.522
"	O< (ethers)	1.639
"	O'' (keto)	2.189
Chlorine	Cl	5.933
Bromine	Br	8.803
Double bond	=	1.686
Triple bond	≡	2.328

TABLE L

	<i>Ma.</i>		Difference.
	Obs.	Calc.	
(Isolated) Diallyl, CH ₂ : CH.CH ₂ .CH ₂ .CH : CH ₂ .	28.77	28.78	- 0.01
(Cumulated) Valerylens, (CH ₃) ₂ C : C : CH ₂ .	24.34	24.18	+ 0.16
(Conjugated) Isodiallyl, CH ₃ .CH : CH.CH : CH. CH ₃	29.87	28.78	+ 1.09
(Twice conjugated) Hexatriene, CH ₂ : CH.CH : CH.CH : CH ₂ .	30.58	28.28	+ 2.30

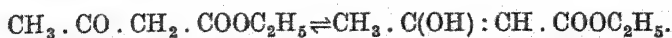
Ring formation seems to exert little influence, at any rate, where the members of the ring exceed four in number. A peculiar point is that the value for the double bond varies with the arrangement of the double bonds in the compound. A compound containing conjugated double bonds, i.e., the grouping —C=C—C=C— , has a higher refractivity than that calculated from the ordinary constants. This "exaltation", as it is called, is characteristic of compounds containing the conjugated double bond. When two double bonds occur together, i.e., when they are cumulated, there is also a difference in the value.

It is to be noted that optical exaltation has not been observed in benzene, although it would appear to have a series of conjugated double bonds. At one time this was used as an argument against



the Kekulé formula in favour of the centric formula, but it has since been shown, on comparison with other ring compounds containing a conjugated system, that benzene is no exception to the general rule.

The property of refractivity has been useful in providing evidence for the formulae of some compounds belonging to the terpene and camphor class, and also in studying the phenomenon of dynamic isomerism such as exists in keto-enol isomerism as typified by acetoacetic ester, $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$.



The results have not, however, proved entirely trustworthy. Calculations of the quantities of the two forms present in the equilibrium mixture based on refractivity do not agree with those obtained by chemical or other physical means. Hantzsch has also applied refractivity to the study of salt formation with the pseudo acids.

(d) ABSORPTION OF LIGHT

Although not strictly a property of liquids alone, the study of light absorption, as far as it concerns chemical constitution, is best taken here. Further mention of this subject will be made in the chapter on Photochemistry (Chapter XIX.).

189. Absorption Spectra and their Determination.—When a beam of white light is passed through a prism it is broken up into its constituent colours, owing to the variation of the refractive index of the glass for different coloured lights, a spectrum being formed. If now some transparent substance, solid, liquid, or gas, is placed in this spectrum, certain parts of the spectrum will be absorbed, and where this occurs dark bands, known as absorption bands, will appear. Thus, if a substance absorbs orange light, this part of the spectrum will be reduced in intensity in the light which has passed through the substance. We say that the substance has an absorption band in the orange.

Absorption bands are studied by means of an instrument called a spectrophotometer, which will give in addition to the position of the bands their relative intensities. The Beckmann quartz spectrophotometer will be described: this is one of the most widely used photoelectric spectrophotometers. The essential parts are shown in Fig. 119. Light enters from a source L. This source may be an ordinary tungsten filament incandescent lamp for the visible, near ultra-violet and infra-red regions, a hydrogen discharge tube in the ultra-violet region, and mercury vapour lamps when very high levels of illumination are desired. The light is reflected from mirror A to mirror B, through a variable slit S, then on to a concave mirror C and reflected from there

on to a quartz prism with a reflecting back surface. A beam of monochromatic light is then reflected from the prism back on to the concave mirror, and thence out through the slit, through the absorption cells and on to a photo-electric tube P. This tube measures the amount of light transmitted. By rotating the prism, light of various wavelengths can be passed through the cells. A cell containing the solvent being used is first placed in the path of the beam, followed by a cell containing the solution of the substance under examination. This procedure enables us to eliminate the absorption due to the solvent. This is carried out for a series of wavelengths. We can then find how the absorption of the substance varies over the range of wavelengths being studied.

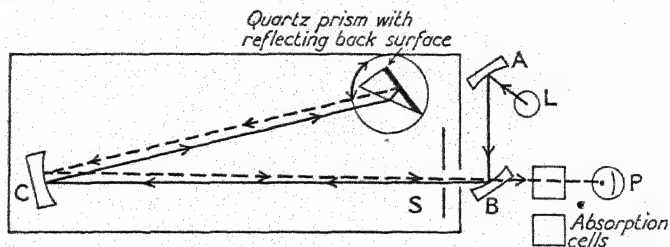


FIG. 119.

This instrument has a variable slit. The range is from 220 to 1,000 $M\mu$ and to cover this range two light sources are employed, a hydrogen discharge bulb for the range 220 to 320 $M\mu$ and a tungsten bulb for the range 320 to 1,000 $M\mu$. The hydrogen discharge bulb is operated from an electronically controlled voltage supply, and the tungsten bulb is operated from a storage battery. The measuring tubes are vacuum photoemissive type cells; two different tubes are used to cover the range of the instrument.

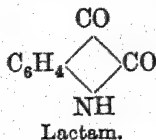
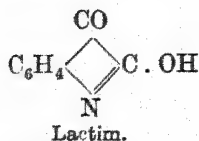
It is found that every substance absorbs light of some wavelength. The range of wavelengths absorbed is called an absorption band.

190. Absorption Spectra and Chemical Constitution.—The relationship between colour and chemical constitution is a question which cannot be studied here. It is our purpose to note some examples of the use of the absorption spectrum in helping to decide questions of constitution.

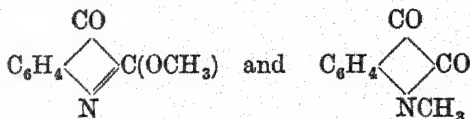
In the first place it must be said that at present we have no method of stating *a priori* what the absorption spectrum of a given compound is going to be like. The only way in which the absorption spectrum can be used is by a comparative method. It has often been found that substances of similar constitution have similar absorption spectra (Hartley's rule). For example, all the permanganates in solution show similar absorption bands; methyl and ethyl esters usually have very similar absorption spectra, and so on. Hence if it is found that two substances

have similar absorption spectra, it is usually safe to say that they also have similar constitutions. In this way the study of absorption spectra has proved of considerable value in deciding questions of structure.

A few examples may be taken. First of all, consider the substance isatin, the oxidation product of indigo. This almost colourless substance may, according to its chemical properties, be regarded as possessing a lactim or a lactam structure. The two formulæ are given below.



Two isomeric methyl derivatives of isatin are known. Their formulæ are



It is known that the introduction of a methyl group into a molecule makes very little difference to the absorption spectrum. The absorption spectrum of the second methyl derivative resembles that of isatin very closely. Hence it is argued that isatin has the formula II, *i.e.*, it has the lactam structure.

This method has also been of use in the determination of the structure of the alkaloids, such as cotarnine and hydrastine.

Hartley, Dobbie, and Lauder studied keto-enol tautomerism by this means, and were able to show, by comparing its absorption spectrum with that of its methyl ether, that phloroglucinol, which sometimes acts as a phenol and sometimes as a ketone, exists almost entirely in the phenolic form in the free state.

There are many other cases of the use of absorption spectra in deciding constitution, but for these the larger text-books or monographs should be consulted.

F. THE MOLECULAR WEIGHTS OF LIQUIDS

191. The Determination of the Molecular Weight of a Liquid.—It is a matter of some difficulty to determine the molecular weight of a liquid. Whilst the molecular weight of a vapour or a gas is readily determined by finding its density and applying the corrected Avogadro Hypothesis, no such method is available for the determination of the molecular weight of a substance in the liquid state. In order to do this it is necessary to make use of some of the properties already mentioned.

One method is to make use of the equation of Ramsay and Shields (§ 177), connecting molecular surface energy with temperature.

$$\gamma \left[\frac{M}{D} \right]^{\frac{2}{3}} = k (T_c - T - 6).$$

The value of k for a number of liquids was found to be 2.12, and as so many gave this value, it was assumed that these were normal liquids. Some liquids, however, give a value for k less than 2.12, and these are supposed to be associated, *i.e.*, their molecular state consists of aggregates of simple molecules. If x is the degree of association (*i.e.*, the aggregates consist of x simple molecules), then Mx is the molecular weight of the substance, and presumably, if this is used instead of M , the Ramsay and Shields' equation should be obeyed. Hence

$$\gamma \left[\frac{Mx}{D} \right]^{\frac{2}{3}} = 2.12 (T_c - T - 6).$$

Thus x can be found.

In this way, the molecular weight of water has been shown to agree with the formula $(H_2O)_3$ at certain temperatures. The molecular complexity decreases as the temperature rises, as is shown in the accompanying table. At 60° C. water would appear to be $(H_2O)_3$; at 20° C. it is clearly a mixture of $(H_2O)_3$ and some higher molecular aggregates.

By this method a number of liquids have been found to be associated as shown in Table LI. (II.).

TABLE LI.—(I.)—DEGREE OF ASSOCIATION OF WATER

Temp. °C.	0	20	40	60	80	100
x	3.81	3.55	3.18	3.00	2.83	2.66

Some objections have recently been made concerning the use of the Ramsay and Shields' equation for this purpose. Some observers urge the approximate nature of the Ramsay and Shields' equation, but a far more important objection is that brought forward by Dutoit and Mojoiu. The surface tension measures conditions at the surface of a liquid and not in its interior. It has been shown by Gibbs and others (§ 360) that these surface conditions are quite abnormal. Thus, in dealing with a solution, the concentration of solute is not the same at the surface as in the bulk of the liquid. Hence it is justifiable to assume that there will be a difference of molecular weight at the surface of a liquid, and this would be the one measured by the Ramsay and Shields' equation. It cannot be argued that if a liquid is associated at the surface it will be associated in the interior of the liquid.

A further objection is the fact that it is definitely known that certain liquids which would not be expected to be associated give values for k which are somewhat removed (both above and below) from the value 2.12.

The general conclusion is, therefore, that it is not safe to argue about

TABLE LI (II.)—ASSOCIATION OF LIQUIDS

Substance.	Temp. Interval. ° C.	Degree of Association.
Methyl alcohol	16-78	3.43-3.24
Ethyl alcohol	16-78	2.74-2.43
Acetic acid	16-132	3.62-2.77
Phenol	46-184	1.42-1.18
Phosphorus	78-132	3.76
Sulphur	115-160	6.00
Nitrogen dioxide	2-20	2.02
Sodium nitrate	300-400	10.68
Potassium nitrate	341-407	8.73

the actual degree of association from the Ramsay and Shields' equation, though it may be used to show the existence of association from the qualitative point of view.

Several other methods of deciding whether a liquid is associated or not are based on surface tension. The parachor has already been referred to (§ 178). It will be remembered that this constant is defined by the equation

$$[P] = \frac{M\gamma^{\frac{1}{4}}}{(D - \bar{d})}$$

which involves the molecular weight. If the constituent groups of the molecule of a compound are known, its parachor can be calculated from the table of constants which has been drawn up. The parachor can also be found from the above equation. If the two values agree, the substance is normal; if not, it is abnormal. Unfortunately this method requires the knowledge of the constitution of the substance before anything can be done, and hence is of little use for determining the molecular weight of an unknown liquid.

Most normal liquids obey Trouton's Rule, which states that

$$\frac{Ml}{T} = \text{const.} = 21,$$

where M is the molecular weight, l the latent heat of evaporation, and T the boiling point of the liquid on the absolute scale. Abnormal liquids deviate considerably from this rule. However, the rule is not sufficiently accurate to enable a direct determination of the molecular weight to be made.

The molecular volume, which is an additive property, may be used in a similar way to the parachor to find out whether a liquid is associated, but it is not of any use in determining the amount of association. The structure of the substance must be known, when the molecular volume

can be calculated from the list of constants drawn up. The molecular volume can also be obtained by experiment. A comparison of the two will give some idea as to whether the liquid is normal.

Sometimes certain physical properties of a liquid give a hint as to their complexity. If we take water as an example we find that it contracts on heating from 0° C. to 4° C., but above this temperature it expands. It is clear that near this temperature, 4° C., there is some alteration in the equilibrium between the liquid molecules.

Ramsay and Young's rule concerning the boiling points of related liquids may be used for detecting association (§ 169).

It was also remarked in connection with viscosity that the ratio

$$\frac{d}{M} \cdot \eta \times 10^6,$$

where d is the density, η the coefficient of viscosity, and M the molecular weight (apparent), comes out between 40 and 60 for normal liquids, whereas for associated liquids the value is considerably higher. This can be used as a criterion of association (§ 182).

192. Some Properties of Associated Liquids.—Many of the liquids which have been shown by various methods to be associated, are found to possess certain properties in common.

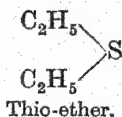
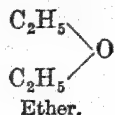
In the first place, associated liquids frequently contain the hydroxyl group. The reason why association takes place when this group is present is probably because the OH group possesses both donor and acceptor properties (§ 75), and because of the readiness with which hydrogen bonds are formed (§ 85). The OH group can therefore co-ordinate with itself. The association, where it exists in these cases, depends upon the presence of both the hydrogen and the oxygen of the hydroxyl, for if one of them is absent the liquid behaves normally. Thus, ether (C_2H_5)₂O, which contains only the oxygen, is not abnormal; ethyl alcohol is. The compound C_2H_6 , H or ethane, is normal.

It is found that associated liquids fall into two classes; those where the association factor appears to be limited to two, and where the limit is nearly reached at comparatively low concentrations, when the substance is dissolved in non-associating solvents; and those where the association factor is much higher, but the association is much less in dilute solution. Examples of the first class are the carboxylic acids, and of the second the alcohols and phenols. The carboxylic acids, such as acetic, seem never to be associated to aggregates containing more than two simple molecules, whereas the alcohols and phenols form larger aggregates.

Associated liquids are usually miscible in all proportions with each other, but not with normal liquids; similarly normal liquids are usually completely miscible with each other, but not with associated liquids. Thus the associated liquids water and ethyl alcohol are miscible in all proportions; the normal liquids ether and benzene are completely miscible, but water and benzene are not miscible.

Associated liquids have all the properties of co-ordinated compounds, as would be expected if the theory that association is due to the presence of both donor and acceptor properties in the molecule is true. Especially do they possess low volatility and high dielectric constants.

If water were a normal liquid, its boiling point would be very much lower than it is. It is known that the ethers boil at temperatures about 60° C. lower than the thio-ethers. The latter compounds are related to the former by the fact that they are ethers, the oxygen of which has been replaced by sulphur.



Now, if we apply this to the case of water, we find that sulphuretted hydrogen boils at - 60° C. Hence water should boil at - 120° C., if it were normal. Its true boiling point is, of course, 100° C., 220° C. more than that calculated on the assumption that it is normal. We are therefore justified in saying that it is an abnormal liquid, and that it is much less volatile than it would otherwise be.

TABLE LII

Associated Liquids.	Dielectric Constant	Normal Liquids.	Dielectric constant
Water	81	Carbon tetrachloride	2
Formic acid	58	Acetic anhydride	21
Methyl alcohol	33	Benzene	2
Acetamide	59	Ether	4
Acetic acid	6	Nitrobenzene	36
Ethyl alcohol	27	Carbon disulphide	3
Amyl alcohol	16	Chloroform	5
Glycerol	39	Ethyl acetate	6

Table (LII.) above gives the dielectric constants of some compounds. It is noticed that those of suspected associated liquids are considerably greater than those of normal liquids. Nitrobenzene and acetic acid are exceptions.

Associated liquids are found to be good ionising solvents. This is partly due to their high dielectric constant which weakens the attractive forces between the ions and facilitates their separation (see § 302).

193. Structure of Liquids.—Most of the properties of liquids may be placed in two categories: properties in which the liquid resembles a gas and properties in which a liquid resembles a solid. Liquids are similar

to gases in their lack of resistance to shearing forces; neither liquids nor gases have a fixed shape but take up the shape of the vessel which they occupy. The resemblance of liquids to solids is shown by the similarity in density and compressibility. We can say, therefore, that the behaviour of liquids is intermediate between that of gases and solids. The structure of liquids shows the characteristics both of solids and gases.

Density determinations for a gas at room temperatures and normal pressures show that the average distance between molecules is of the order of 20 \AA .; for solids the average distance is of the order of 3 \AA ., and for liquids a little over 3 \AA . An important consequence of this is that while intermolecular forces need not be considered in an approximate treatment of gases the same is not true for liquids. Because of this we can regard the structure of liquids as involving molecules being packed together in a manner somewhat similar to the molecules of a solid. However, the structure adopted must be such that the properties of flow can be explained. To do this it is necessary to assume that in a liquid a few molecules can move at a time. This requires the assumptions that groups of molecules associate together leaving spaces in parts of the lattice, and that though the pattern of molecules is regular, in the immediate neighbourhood of a given molecule the pattern may be irregular at a distance from this molecule.

Liquids like solids give X-ray diffraction patterns and these indicate that the above conclusions on liquid structure are approximately correct. Starting with a particular molecule the liquid structure is a rather irregular version of a solid structure, at least in the region of a few diameters of the given molecule. In a liquid a molecule has a tendency to surround itself with a definite number of neighbouring molecules, and as a result in a small region there will be a regular arrangement of molecules. As the size of the region is increased irregularities increase and the position of molecules through the region is not determined by a regular sort of arrangement. Thus there is no long-range order in a liquid as there is in a solid. In a solid the position of molecules many diameters from a central molecule can be predicted from a knowledge of the central molecule and the molecules immediately surrounding it. The order that exists in the immediate neighbourhood of a molecule in a liquid is called short-range order.

The X-ray work on liquids also establishes the existence of holes; these are definite gaps in the packing of atoms; holes are also present in solids but in smaller numbers than in liquids. The presence of these holes permits the molecules in the liquid to move about and hence the fluidity of a liquid depends more or less directly on their presence.

The structure of liquids may be studied theoretically on the basis of the loose packing of spheres. When spheres are packed carefully to occupy a minimum volume a regular arrangement is obtained, which is

the basis of the structure of solids. In a liquid the spheres are regarded as being packed loosely, that is in a volume greater than the minimum necessary volume and the arrangement of spheres so obtained is not regular. By considering the loose packing of spheres it is possible to get agreement with the X-ray data for liquids. Thus liquids may be considered as imperfect crystals (as crystals with holes) and on the basis of this model the process of the evaporation of a liquid can be accounted for theoretically. The model, however, will not account for the process of fusion. The hole model of a liquid is improved by the free volume model which considers the molecules of a liquid as being confined within a small volume by surrounding molecules. Within this confinement a molecule is free to move as a molecule of an ideal gas. The volume available to the centre of an average molecule in its motion is called the free volume. The free volume is not the volume of the hole in which the molecule moves, for the molecule occupies a finite space. Nor is it the volume of the hole minus the volume of the molecule for there are crevices between the neighbouring molecules into which the central molecule cannot squeeze. It is best to regard free volume as something to be determined experimentally. The free volume model enables us to describe the process of fusion as well as that of evaporation.

The theories described above consider a liquid as an imperfect solid. A liquid may also be considered as an imperfect gas. Such a theory which considers the effect of intermolecular forces of attraction and repulsion that operate within a liquid has been applied to the theory of condensation with some success.

The structure of water has been studied by X-ray methods. In ice each oxygen atom is tetrahedrally attached to four other oxygen atoms by means of hydrogen bonds. The structure is not a close packed one. Melting leads to the breaking of the ice structure with fission of some hydrogen bonds. The fragments resulting tend to pack as closely as possible. As a result some of the oxygen atoms have more than four molecules packed around them; they increase their quota of nearest neighbours. This leads to an increase in density. As the temperature increases, the increase of density due to a breaking of bonds will continue. However, the effect is outweighed by an increase of thermal agitation with temperature with a consequent decrease in density.

SUGGESTIONS FOR FURTHER READING

- YOUNG, S. "Stoichiometry." (*Longmans*.)
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SUGDEN, S. "Parachor and Valency." (*Routledge*, 1930.)

CHAPTER X

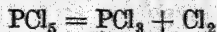
CHEMICAL KINETICS AND EQUILIBRIUM

194. Velocity of Reaction.—Every chemical reaction under specified conditions of temperature, concentration, etc., proceeds at a definite speed. The majority of inorganic reactions, namely, those which take place between ions, proceed very rapidly, and would commonly be called instantaneous. Actually, however, they each have a definite speed. Most organic reactions, which take place between covalent compounds, proceed much more slowly.

The speed of a reaction may be defined as the weight of the reactants transformed, in gram-molecules, per second (see also § 196).

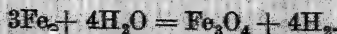
There are a number of factors which alter the speed of a reaction. They are temperature, concentration, and catalysis, although there may also be others, such as surface tension.

195. Reversible Reactions. The Nature of Equilibrium.—It has been known for some time that many chemical reactions do not go to completion as indicated by the equations representing them. Thus, when phosphorus pentachloride is heated in a closed vessel, the reaction



takes place; but the pentachloride is not entirely converted into trichloride and chlorine. At a certain stage in the process, the reaction stops and a mixture of the pentachloride, trichloride, and chlorine is obtained. If some phosphorus trichloride, together with an equivalent quantity of chlorine, is heated in a closed vessel to the same temperature as the pentachloride in the first experiment, it will be found that some phosphorus pentachloride is formed, and, at the same temperature, the final composition of the mixtures in both experiments will be the same. It would therefore appear that the phosphorus trichloride is recombining with the chlorine as fast as the pentachloride is decomposing. When this occurs there is a state of equilibrium. Reactions which can proceed in both directions according to the experimental conditions are called "reversible reactions".

Another common example of a reversible reaction is the action of steam on red-hot iron. It is well known that hydrogen is prepared by this method, and that the residue is ferrous-ferrous oxide, Fe_3O_4 .



If this reaction were to be carried out in a closed vessel, as it could, for example, if water were heated in an iron vessel which would withstand

the pressure, it would be found that it does not proceed to completion, but that only a certain proportion of the water is converted into hydrogen. If the reverse reaction were carried out, at the same temperature as before, and under exactly the same conditions, it would be found that the composition of the equilibrium mixture would be the same. Hence, although the reaction comes to a standstill, this is only an apparent standstill. Actually the reactions are proceeding all the time, but the forward reaction is going on at exactly the same rate as the backward. There is thus no actual stoppage of the reaction. In the ordinary laboratory preparation of hydrogen by passing steam over red-hot iron, the back reaction is not permitted to occur, for the hydrogen is swept out of the apparatus by the oncoming steam, and prevented from reacting with the ferrous-ferrie oxide formed. Similarly with many other reactions. It is necessary to take careful consideration of the conditions of a reaction before saying whether it will proceed in the forward direction, in the backward direction, or both simultaneously.

It has been said that all chemical reactions are reversible. This may be true if these reactions may be carried out under any chosen conditions, but the majority of chemical reactions, as they are performed in the laboratory, proceed in one direction only. The precipitation of barium sulphate by adding sulphuric acid to barium chloride, although it may appear to be irreversible, is certainly a reversible reaction, because if barium sulphate is treated with hydrogen chloride a small quantity of barium chloride and sulphuric acid may be produced. In carrying out reactions in the laboratory, one is careful to obtain the greatest yield of the substance required by so defining the conditions that the back action is minimised. Thus, in the preparation of an organic ester, it is well known that the action of an acid on an alcohol yields an ester and water, but that the ester may also be hydrolysed back to the acid and alcohol from which it was made by boiling with water. Here then we have a reversible reaction, but care is taken to get as great a yield of ester as possible in the reaction by removing the water from the ester as soon as it is formed. This is accomplished by adding to the reaction mixture some dehydrating agent, such as zinc chloride, or concentrated sulphuric acid. In this way the back reaction is prevented.

Thus, whilst it is true that all chemical reactions may be made reversible by choosing the conditions correctly, so it is also true that a reaction may be made to proceed to completion, or very nearly so, by preventing the back reaction from taking place.

196. The Law of Mass Action.—The causes of chemical action attracted a number of the more thoughtful chemists in the late eighteenth century. The question of chemical affinity was beginning to be studied, in an empirical way, at this time, and in 1775, Bergmann published a "Table of Affinities". In this he showed that he realised

that reactions could be reversible, and hence that affinities could actually be reversed. He published a list of "affinities of elements in fire", and "in water". In 1777, Wenzel suggested that the rate of a chemical reaction did not depend only on the affinities of the combining substances, but also on their quantity. This suggestion, which might have been very fruitful, was, however, ignored. In 1799, Berthollet explained the formation of sodium carbonate in certain Egyptian lakes by the interaction of calcium carbonate and sodium chloride. In the laboratory calcium chloride and sodium carbonate give a precipitate of calcium carbonate, and the solution contains sodium chloride. These two reactions are exactly the reverse of each other, but Berthollet maintained that the first could go on if the quantity of the sodium chloride, or of the calcium carbonate (in solution), were sufficiently large, and these conditions were found in these lakes. He stated that increase in mass could overcome weakness of affinity. He was, however, wrong in stating that the quantity of substance present could affect the ratio in which the substances combine. This was against the Law of Constant Proportions, which had just been propounded. Berthollet, however, did not believe in the truth of this law, as was mentioned in Chapter I.

Later, investigations were made of the rates of chemical reactions. Wilhelmy was the first to do this in 1850. In 1862, Berthelot and St. Gilles investigated the equilibrium between ethyl alcohol, acetic acid, ethyl acetate, and water, and arrived at conclusions which were embodied by Guldberg and Waage in their "Law of Mass Action", in 1864.

Guldberg and Waage stated that "*the rate at which a substance reacts is proportional to its active mass*". The "*velocity of a chemical reaction is proportional to the products of the 'active masses' of the reactants*".

What is meant by the "active mass" of the substance? The "active mass" was assumed by Guldberg and Waage to be proportional to the molecular concentration in the case of gaseous and dissolved substances. The molecular concentration is the concentration expressed in gram-molecules per litre, and, since a gram-molecule of every substance contains the same number of molecules, concentrations expressed in this way indicate the number of molecules present.

Take the reaction,



(The symbol \rightleftharpoons indicates that the reaction is reversible.)

The velocity of the forward reaction is proportional to the molecular concentration of A and to that of B, and hence is proportional to their product. Molecular concentrations are represented by symbols in square brackets; thus [A] represents the molecular concentration of A. The velocity of the forward reaction is thus

$$V_f = k_1 [A] [B].$$

Similarly, the rate of the backward reaction is given by

$$V_b = k_2 [C] [D].$$

At equilibrium these two rates are the same, since as much of the products are formed as are decomposed in the same time; hence

$$\begin{aligned} V_b &= V_f; \\ k_2 [C] [D] &= k_1 [A] [B], \\ \frac{k_1}{k_2} &= \frac{[C] [D]}{[A] [B]} = K. \end{aligned}$$

K is called the *equilibrium constant* of the reaction, and k_1 and k_2 are called *velocity constants*.

Ray 197. **Derivation of the Law of Mass Action on the Basis of the Kinetic Theory.**—According to the kinetic theory, substances are made up of molecules in motion, and chemical combination does not occur unless two molecules collide. Combination does not take place at every collision. Many of them are quite ineffective. Not one collision in a million results in combination, in reactions which take place at a measurable speed. However, the number of effective collisions is a definite fraction of the total (§ 214).

It is clear that the number of collisions, and the number of effective collisions, will be increased, the greater the number of molecules present, i.e., the greater the concentration. Thus, the rate of the reaction will be proportional to the molecular concentration of the reactant. Where reaction is taking place between two dissimilar molecular species, collision must occur between two molecules of the different types, and the probability of this will depend on the concentration of both. This probability will be given by the product of the two concentrations. Hence, the velocity of the reactions is proportional to the product of the molecular concentrations of the two species, which is the Law of Mass Action.

The law may also be proved by thermodynamics (§ 113).

198. **Some Examples of the Application of the Law of Mass Action.**—Consider first the rate of formation of ethyl acetate from ethyl alcohol and acetic acid. The equation is



Hence, the rate of formation of ethyl acetate and water is given by

$$V_f = k_1 [\text{CH}_3 \cdot \text{COOH}] [\text{C}_2\text{H}_5\text{OH}].$$

The reverse reaction will also go on, unless steps are taken to remove the water, or the ester, as it is formed. The rate of the reverse reaction is given by

$$V_b = k_2 [\text{CH}_3 \cdot \text{COOC}_2\text{H}_5] [\text{H}_2\text{O}].$$

At equilibrium the rates are equal ; hence

$$V_b = V_f;$$

$$k_1 [\text{CH}_3 \cdot \text{COOH}] [\text{C}_2\text{H}_5\text{OH}] = k_2 [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}],$$

$$\therefore K = \frac{k_1}{k_2} = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]}{[\text{CH}_3 \cdot \text{COOH}] [\text{C}_2\text{H}_5\text{OH}]}$$

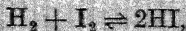
The equilibrium constant is K .

It is usual to write in the numerator the active masses of the products, and in the denominator those of the reactants. The value of K for the above reaction is 4 at 25° C.

In all determinations of equilibrium constants care must be taken to see that the equilibrium does not alter during, or as a result of, the analysis of the equilibrium mixture. In many cases of reaction at fairly high temperatures the reactions will proceed very slowly at room temperature, so that sudden cooling of the reaction mixture will stop the reaction, and the proportions of the substances present will be those obtaining at the higher temperature. This is called "freezing the equilibrium". It may be mentioned in passing that this process is one of great importance. The reason why endothermic substances like ozone are stable at room temperatures is because they are in such a state that the equilibrium has been frozen. Ozone is formed at very high temperatures. The passage of the silent discharge through oxygen is merely the addition of a large amount of energy to the oxygen, in another way than by direct heating. If oxygen, then, is heated to extremely high temperatures, some ozone will be formed. If the reaction mixture were to be cooled to room temperatures suddenly, the equilibrium would be frozen, and the amount of ozone present would be the same as if the gas were kept at the high temperature. Of course, it is useless to bring about the cooling slowly, for this will allow time for the reactants to alter their equilibrium.

The combination of hydrogen and iodine to form hydrogen iodide has been studied by Bodenstein. All that is necessary is to heat the hydrogen and iodine together, in various proportions, in sealed tubes, to a temperature about 450° C. After a time, sufficiently long for equilibrium to be attained, the tubes are suddenly cooled, and the amount of hydrogen left determined by absorbing the iodine and hydrogen iodide in potassium hydroxide. The amount of hydrogen iodide and of iodine are determined in the liquid obtained by absorption by the usual methods of volumetric analysis.

In an actual experiment, it was found that when 20.55 gm.-mols. of hydrogen were heated to 445° C. with 31.89 gm.-mols. of iodine, the equilibrium mixture contained 2.06 gm.-mols. of hydrogen, and 13.40 gm.-mols. of iodine, and 36.98 gm.-mols. of hydrogen iodide. The reaction is



and the mass action equation is,

$$K = \frac{[\text{HI}][\text{HI}]}{[\text{H}_2][\text{I}_2]} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}.$$

Substituting the values

$$K = \frac{(36.98)^2}{2.06 \times 13.40} = 49.5.$$

Hence the equilibrium constant is 49.5.

Of course, if different initial concentrations are taken, different values for the quantities of substances formed will be obtained, but the equilibrium constant will still be the same at the same temperature. This can be tested by repeating the experiment with different quantities. The following are some of the results obtained.

TABLE LIII.—THE HYDROGEN IODIDE EQUILIBRIUM
(Bodenstein)

Initial Concentrations. gm.-mols.		Final Concentrations. gm.-mols.			K.
H ₂	I ₂	H ₂	I ₂	HI	
20.57	5.22	15.46	0.11	10.22	61.44
20.6	14.45	7.79	1.64	25.72	51.77
20.55	31.89	2.06	13.40	36.98	49.55
20.41	52.8	1.07	33.46	38.68	41.8
20.28	67.24	0.52	47.48	39.52	63.3

The values of K have been calculated from

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}.$$

Although K appears to vary considerably, the unavoidable experimental error is great. Any error in the concentration of hydrogen iodide is squared, so that the above figures may be taken as a satisfactory indication that the reaction follows the law.

If only the initial concentrations of hydrogen and iodine and the concentration of hydrogen iodide formed are known, the equilibrium constant can still be calculated. The procedure, which is quite general, is as follows. Consider the reaction



Let $2x$ gm.-mols. of hydrogen iodide be produced, and let a be the initial concentration of hydrogen in gm.-mols. per litre, and b the initial concentration of iodine in gm.-mols. per litre (at the temperature of the experiment this iodine will be in the vapour state). The volume

of hydrogen iodide formed is not different from the total volume of the gases from which it was formed. Since $2x$ gm.-mols. of hydrogen iodide are produced for x gm.-mols. of hydrogen and x gm.-mols. of iodine used up, the final concentration of hydrogen will be $(a - x)$ and of iodine $(b - x)$ gm.-mols.

Substituting these values in the mass equation, we have

$$K = \frac{4x^2}{(a - x)(b - x)}$$

If we know x , a and b , we can then calculate K . Thus taking as a numerical example the first set of data given in the table above:—

Initial concentration of hydrogen = $20.57 = a$.

Initial concentration of iodine = $5.22 = b$.

Concentration of hydrogen iodide at equilibrium = $10.22 = 2x$.

$$\therefore a - x = 20.57 - 5.11 = 15.46$$

$$b - x = 5.22 - 5.11 = 0.11$$

$$\therefore K = \frac{4x^2}{(a - x)(b - x)} = \frac{(10.22)^2}{15.46 \times 0.11} = 61.44$$

In examples involving gaseous equilibria, the concentrations of the reactants are frequently expressed as their partial pressures. These are of course equivalent to the concentrations.

199. The Effect of Pressure on Chemical Equilibrium.—It is molecular concentration that enters into the mass equation. If pressure is applied to a system, the volume becomes smaller, and the molecular concentrations of the constituents are increased. If there is no volume change in the reaction, the equilibrium will not be altered in any way, for the concentrations of products and reactants will be affected in the same proportion; but, if there is a volume change in the course of the reaction, that reaction will be favoured which takes place with decrease in volume. This also follows from the principle of Le Chatelier, which states that if any constraint is applied to a system in equilibrium the equilibrium is shifted in such a way as to annul, or tend to annul, the constraint. In this case the constraint is the application of pressure. The reaction which results in decrease in volume will therefore take place, for by itself decreasing the volume the system tends to annul the effect of the pressure.

Consider the dissociation of phosphorus pentachloride. It takes place according to the equation



Suppose there are initially a gram-molecules of phosphorus pentachloride in a volume V litres. The reaction is supposed to be carried out in closed vessels, so that V remains constant. If there are x gram-molecules of phosphorus trichloride formed, it follows from the equation that there will also be x gram-molecules of chlorine formed. The

molecular concentration of the pentachloride at equilibrium will therefore be $(a - x)/V$, whilst that of the trichloride and of chlorine will be (x/V) . Hence, applying the mass law,

$$K = \frac{\left(\frac{x}{V}\right)^2}{\frac{a-x}{V}} = \frac{x^2}{(a-x)V}$$

It will be noticed that V occurs in the denominator. Hence the greater V is, the greater $\frac{x^2}{a-x}$ will be, for the constant K must be maintained.

This means that the amount of dissociation, x , must be greater. Hence the diminution of pressure (*i.e.*, increase in volume, V , since it is only by increasing the volume that the pressure can be reduced without removing some of the reactants from the system) in this system results in an increase in the dissociation, and conversely.

Where V disappears in the mass equation, pressure, of course, has no effect on the equilibrium. Thus, in the dissociation of hydrogen iodide, there is no change in volume, and so V does not figure in the mass equation, and pressure alterations have no effect on the equilibrium.

This effect of pressure on the position of equilibrium is of great importance in technical processes. In the Haber synthesis of ammonia, the reaction is,



Four volumes of the mixed nitrogen and hydrogen give only two volumes of ammonia. Hence the formation of ammonia will be favoured by the application of pressure, and in practice, in the Haber process, a pressure of 200 atmospheres is used, whilst in the Claude process a pressure of 1,000 atmospheres is employed.

In some cases it is found uneconomical to work at high pressures, although better yields would result. Thus in the Contact process for the manufacture of sulphuric acid by making sulphur dioxide combine with oxygen, the reaction is



and involves a decrease in volume. Hence it would be favoured by the application of pressure. This is not done, however, in practice, owing to the difficulty of making acid-proof apparatus suitable for working at high pressures, and also because a sufficiently good yield may be obtained without recourse to the application of pressure.

A quantitative example of the effect of pressure on the equilibrium may be found in the Haber synthesis of ammonia. The effect of pressure on the yield of ammonia will be calculated. The reaction is



At a given temperature, let the partial pressures of nitrogen, hydrogen

and ammonia in the equilibrium mixture be p_{N_2} , p_{H_2} and p_{NH_3} . Then, by the Law of Mass Action,

$$\frac{p_{NH_3}^2}{p_{N_2} \cdot p_{H_2}^3} = K. \therefore p_{NH_3}^2 = K \cdot p_{N_2} \cdot p_{H_2}^3 \quad (1)$$

Now double the pressure on the system. If it is assumed that the partial pressure of the ammonia is small compared with that of nitrogen and hydrogen and the small amount of extra ammonia formed does not affect the partial pressures of the other gases—a condition which always holds in technical practice—then the partial pressures of hydrogen and nitrogen will be doubled.

Let the new equilibrium pressures be p'_{N_2} , p'_{H_2} , and p'_{NH_3} . Then

$$\frac{p'^2_{NH_3}}{p'_{N_2} p'^3_{H_2}} = K = \frac{p^2_{NH_3}}{2p_{N_2} \cdot 8p^3_{H_2}},$$

$$p'^2_{NH_3} = 16p_{N_2} \cdot p^3_{H_2} \cdot K = 16p^2_{NH_3} \text{ (see equation (1) above).}$$

$$\therefore p'_{NH_3} = 4p_{NH_3}.$$

Thus, the partial pressure of ammonia is four times what it was originally, although the pressure on the system has only been doubled. The amount

of ammonia formed per unit volume of nitrogen is $\frac{2p_{NH_3}}{p_{N_2}}$ in the first case,

and in the second $\frac{2p'_{NH_3}}{p'_{N_2}}$. It will be seen that the yield is double, since

$$p'_{NH_3} = 4p_{NH_3} \text{ and } p'_{N_2} = 2p_{N_2}.$$

200. Effect on the Equilibrium of Adding one of the Products of the Reaction.—To study this question, the dissociation of phosphorus pentachloride may again be considered. It is desired to find what effect there will be on the dissociation if chlorine is added from some outside source to the equilibrium mixture. Writing the equation



suppose we have at equilibrium a gm.-mols. of the pentachloride in V litres, b gm.-mols. of trichloride, and b gm.-mols. of chlorine in V litres. It follows from the equation that the amounts of chlorine and of trichloride must be equal. The mass law gives

$$K = \frac{b^2}{aV}.$$

Suppose now that c gm.-mols. of chlorine are introduced into the system *without change of volume*. Let b' and a' be the new concentrations of the trichloride, and pentachloride, respectively. Then $(b' + c)$ is the new concentration of chlorine, and

$$K = \frac{b'(b' + c)}{a'V}.$$

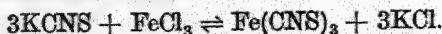
In order to maintain K constant, b must be decreased (to b'), and hence the dissociation will be retarded, some pentachloride being re-formed.

If, however, the chlorine is added with change of volume, it all depends on the volume change what the change in the system will be. If the volume after addition of chlorine is V' , then the mass law states,

$$K = \frac{b'(b' + c)}{a'V'},$$

where a' and b' are the new concentrations of pentachloride and of trichloride. It would be possible to work out the effect in any example in which the concentrations were given.

The effect of the addition of products of reaction on the position of equilibrium is well illustrated by the following experiment due to Gladstone. Consider the reaction



The ferric thiocyanate is deeply coloured. Addition of potassium chloride in saturated solution (to avoid great changes in volume of the solution) makes the reaction mixture become appreciably paler. This is due to the fact that the reverse reaction is favoured, since the value of $[\text{Fe}(\text{CNS})_3]$ in the numerator of the mass action equation

$$K = \frac{[\text{Fe}(\text{CNS})_3] [\text{KCl}]^3}{[\text{FeCl}_3] [\text{KCNS}]^3}$$

must become smaller to make K still constant. On the other hand, addition of ferric chloride causes a deepening of the colour, since the value of the denominator is increased, and consequently the value of the numerator must also be increased to maintain K constant. Similarly, addition of potassium thiocyanate also causes an increase in the depth of colour.

201. The Effect of Temperature on the Equilibrium.—According to Le Chatelier's principle (§ 199), in the case of a reversible reaction, increase in temperature will favour that reaction which takes place with absorption of heat. Decrease in temperature will favour the reaction which takes place with evolution of heat (see also § 95).

It can be shown by thermodynamics (§ 114) that if K_1 and K_2 are the equilibrium constants of a reaction at absolute temperatures T_1 and T_2 , and if ΔH is the heat of reaction expressed in gram-calories absorbed at constant volume,

$$\log_{10} K_2 - \log_{10} K_1 = - \frac{\Delta H}{4.576} \left(\frac{1}{T_2} - \frac{1}{T_1} \right).$$

This equation may be made use of for determining the heat of reaction.

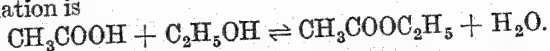
An example of the use of this equation is given below.

202. Some Numerical Examples.—In order that the reader may more fully comprehend the work that has just been described, he is recommended to try to solve the following numerical examples for

himself. The solutions to the problems are also given below so that the work may be checked.

(1) The equilibrium constant in the reaction between ethyl alcohol and acetic acid to form ethyl acetate and water is 4 at 25° C. What weight of ethyl acetate will be obtained from 50 gms. of alcohol and 50 gms. of acetic acid, the reaction being carried out at 25° C. in a closed vessel?

The equation is



According to the Law of Mass Action,

$$\frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{C}_2\text{H}_5\text{OH}][\text{CH}_3\text{COOH}]} = K \quad (1)$$

where the substances in square brackets stand for molecular concentrations.

It is supposed that the total volume of the system, V , does not change during the reaction. Let x be the number of gram-molecules of ethyl acetate formed; then x will also be the number of gram-molecules of water formed.

The molecular weight of acetic acid is 60.05. Hence the molecular concentration of acetic acid was originally $\frac{50}{60.05V}$. If x gram-molecules of products are formed, then x gram-molecules of reactants must have been used up, so the final molecular concentration of acetic acid was $\left(\frac{50}{60.05} - x\right)/V$.

The molecular weight of ethyl alcohol is 46.047. Hence, final molecular concentration of alcohol is $\left(\frac{50}{46.047} - x\right)/V$. Substituting these values in equation (1),

$$\frac{\left(\frac{x}{V}\right)^2}{\left(\frac{50}{46.047} - x\right)\left(\frac{50}{60.05} - x\right)} = K = 4.$$

$$\therefore \frac{x^2}{(1.086 - x)(0.8326 - x)} = 4,$$

$$\therefore x^2 = 4(0.9038 - 1.9186x + x^2),$$

$$3x^2 - 7.6744x + 3.6152 = 0.$$

or

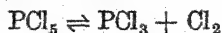
The roots of this equation are

$$x = 1.9747 \text{ or } 0.5834.$$

The first of these is inadmissible, as the quantities of acetic acid and

alcohol taken are insufficient to produce this amount of ethyl acetate, even if the reaction went to completion. Hence 0.5834 gm.-molecules of ethyl acetate will be produced, *i.e.*, $0.5834 \times 88.0624 = 51.39$ gms.

(2) Calculate the percentage dissociation of phosphorus pentachloride in an experiment in which 2.0 gms. of the substance were heated to 200°C . in a closed litre vessel, which contained only phosphorus pentachloride, and the products of the dissociation. The equilibrium constant for the reaction



is 0.00793 at 200°C ., and under the pressure developed in the experiment.

Suppose that initially the quantity of the pentachloride present was a gram-molecules. This dissociates, so that x gram-molecules of both the trichloride and chlorine are formed, leaving $(a - x)$ gram-molecules of the pentachloride undissociated. As the reaction is carried out in a closed vessel, the volume, v , cannot change. By the Law of Mass Action,

$$\frac{x^2}{v(a - x)} = K.$$

Now, in the experiment, $a = \frac{2}{208.255}$ gram-molecules per litre, $v = 1$,

and $K = 0.00793$.

$$\therefore \frac{x^2}{(0.009603 - x)} = 0.00793,$$

$$\therefore x^2 = 0.00007615 - 0.00793x,$$

$$\text{or } x^2 + 0.00793x - 0.00007615 = 0.$$

The roots of this equation are $x = -0.01305$ or $+0.0056$.

The negative value is clearly inadmissible.

$$\text{The percentage dissociation} = \frac{x}{a} \times 100 = \frac{0.0056}{0.009603} \times 100 = 58.32$$

per cent.

(3) The equilibrium constant of the reaction



at 528°C . is 980 , and at 680°C . is 10.5 . Find the heat of reaction.

The equation (§ 201) is

$$\log_{10} K_2 - \log_{10} K_1 = -\frac{\Delta U}{4.576} \left(\frac{1}{T_2} - \frac{1}{T_1} \right),$$

where K_2 and K_1 are the equilibrium constants at absolute temperatures T_2 and T_1 , and ΔU is the heat of reaction at constant volume, which is the charge in internal energy.

$$K_2 = 980; K_1 = 10.5; T_2 = 801^\circ \text{Abs.}; T_1 = 953^\circ \text{Abs.}$$

$$\therefore \log \frac{980}{10.5} = -\frac{\Delta U}{4.576} \left(\frac{1}{801} - \frac{1}{953} \right).$$

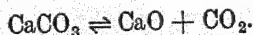
$$\therefore -\Delta U = \frac{953 \times 4.576 \times 801 \times 1.97}{152},$$

$$= -45,280 \text{ gm.-cals.}$$

The amount of heat *given out* is therefore 45,280 gm.-cals.

203. Application of the Law of Mass Action to Heterogeneous Systems.—In the foregoing paragraphs only those reactions which take place in one phase (*i.e.*, homogeneous reactions) have been considered. Many reactions, however, take place between reactants in different phases. These are called "heterogeneous reactions". Numerous reversible heterogeneous reactions are known. Indeed, one of those quoted at the beginning of this chapter as an example of a reversible reaction, *viz.*, the action of steam on red-hot iron, is a heterogeneous reaction. The hydrogen and the steam are gases, whilst the other reactants are solids. Can the Law of Mass Action be applied to a reaction such as this?

The easiest way to consider a reaction of this kind is to assume that it does go on in one phase only. Take the action of heat on calcium carbonate. This is a well-known reversible reaction. If calcium carbonate is heated in a closed vessel, a state of equilibrium is reached after a time, when no more calcium carbonate will decompose. This equilibrium is prevented in a lime-kiln, because it is open and the carbon dioxide can escape as it is formed.



The reaction may be regarded as taking place between calcium carbonate and calcium oxide vapours, and carbon dioxide gas. The concentrations of the reacting substances will be expressed by their partial pressures. If these are p_{CaCO_3} , p_{CaO} , p_{CO_2} , the Law of Mass Action states

$$\frac{p_{\text{CaO}} \cdot p_{\text{CO}_2}}{p_{\text{CaCO}_3}} = K.$$

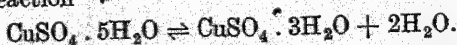
The partial pressure of calcium oxide is its vapour pressure. The vapour pressure of a solid is very small, but, at a given temperature, is constant so long as there is any solid present, so that both p_{CaO} and p_{CaCO_3} are constant, and the law gives us

$$p_{\text{CO}_2} = K'.$$

The system is therefore at equilibrium at a given temperature when a fixed pressure of carbon dioxide is present, a result which is also obtained from Phase Rule considerations (§ 220).

It may be taken as a general rule, when dealing with heterogeneous equilibria, that the active mass of a solid is constant.

The same considerations govern the dissociation of salt hydrates. Consider the reaction



If p_1, p_2, p_3 , are the partial pressures of the pentahydrate, the trihydrate, and water vapour respectively in the system, then

$$\frac{p_2 \cdot p_3^2}{p_1} = K.$$

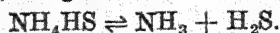
But the active masses of the solids are constant at a given temperature, so long as they both remain in the system.

Hence $p_3^2 = k$,

and $p_3 = \sqrt{k} = k'.$

This result has also been obtained from Phase Rule considerations (§ 220). As soon as one of the hydrates has disappeared, the conditions are altered, for a new equilibrium is set up, and then the partial pressure of the water vapour will be different from before, but will remain constant until the phases again change.

The dissociation of ammonium hydrosulphide, NH_4HS , is a slightly different case. This solid substance dissociates on heating into ammonia and hydrogen sulphide, two gases.



If the partial pressures of the gases are p_{NH_3} and $p_{\text{H}_2\text{S}}$ respectively, then the Law of Mass Action states

$$\frac{p_{\text{NH}_3} \cdot p_{\text{H}_2\text{S}}}{p_{\text{NH}_4\text{HS}}} = K.$$

But $p_{\text{NH}_4\text{HS}}$ is the vapour pressure of the solid, and is constant as long as any solid is present. Hence

$$p_{\text{NH}_3} \cdot p_{\text{H}_2\text{S}} = k'.$$

This equation can be tested by adding one or other of the gases to the system and noting the effect on the equilibrium pressures. The following table gives results of such an experiment:—

TABLE LIV

p_{NH_3}	$p_{\text{H}_2\text{S}}$	$p_{\text{NH}_3} \times p_{\text{H}_2\text{S}}$
mm. 250.5	mm. 250.5	mm. ² 62,750
208.0	294.0	61,150
453.0	143.0	64,780

The volume was kept constant. The product is reasonably constant.

204. Theory of Activities.—In the Law of Mass Action the quantities used are the active masses, which have been stated to be proportional

to the molecular concentrations of the reactants. Owing to intermolecular influences, the freedom of the molecules is always somewhat restricted in actual systems, and the active masses are not proportional to the molecular concentrations. It has therefore been proposed to substitute for the molecular concentration the "activity" of the substance. The activity is a thermodynamic function introduced by G. N. Lewis, and was at first purely formal. As a result of work on electrolytes (§ 321) it has, however, now assumed a more precise significance.

The activity coefficient f is defined as the factor by which the molecular concentration must be multiplied in order that the Law of Mass Action may be obeyed. There are several methods of determining activities, but further discussion of the question is beyond the scope of this book. The concept has found its greatest application in connection with ionic equilibria (§ 321).

✓ **205. The Order of a Reaction.**—The next few sections will be concerned mainly with reaction velocity, and not with reversible reactions. The velocity of reaction is defined as *the rate of change of concentration of the reactants*. The order of a reaction is defined as *the minimum number of molecules necessary for the reaction to take place*. Thus in the reaction



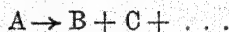
the velocity is given by

$$v = k[A]^l [B]^m [C]^n,$$

and the order is the sum of the indices, $l + m + n$. The order of a reaction only has significance when it is applied to a reaction proceeding in one direction. It is quite possible for a reversible reaction to have two orders, one for the forward, the other for the backward reaction.

✓ **206. Unimolecular Reactions.**—Unimolecular reactions are those in which the reaction velocity is proportional to the first power of the concentration of the reacting substance. They are not so common as they were at first thought to be. Many so-called "unimolecular" reactions were found not to be homogeneous reactions at all, but to take place at the walls of the vessel, or at the surface of some catalyst (see § 207).

A unimolecular reaction may be represented by the equation



If there are present originally a gram-molecules per litre of A , and, after a time t , x gram-molecules are transformed, then the concentration after time t is $(a - x)$. Hence, by the Law of Mass Action.

$$v = \frac{dx}{dt} = k(a - x),$$

or

$$\frac{dx}{a-x} = kdt,$$

which on integration gives,

$$-\log_e (a-x) = kt + C,$$

where C is a constant.

To determine C , it is noted that when $t = 0$, $x = 0$. Substituting these values in the equation, we have

$$-\log_e a = C,$$

$$\therefore k = \frac{1}{t} \log_e \frac{a}{a-x}.$$

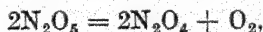
k is, of course, the *velocity constant*.

When the velocity constant of a reaction conforms to this equation the reaction is called a first order reaction. It will be seen that the time taken to complete any definite fraction of the reaction is independent of the concentration. Thus, the time taken for the reaction to reach the half-way stage is found by putting $x = 0.5a$. When this is done,

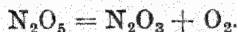
$$k = \frac{1}{t} \log_e 2,$$

which does not involve the concentration.

The number of unimolecular gaseous reactions is very small, and at one time the view was put forward that they did not exist at all. However, a few have now been discovered. They are nearly all confined to molecules of rather complex structure. Until 1925 the only unimolecular reaction known was the thermal decomposition of nitrogen pentoxide. This decomposition is usually expressed in inorganic textbooks by the equation



but, if it is unimolecular, this cannot be the primary change, since this equation involves the participation of two molecules of the substance. The mechanism of the reaction must therefore be somewhat as follows:—



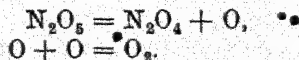
The nitrogen trioxide then decomposes immediately into nitric oxide and nitrogen dioxide:—



The nitric oxide now immediately reacts with the pentoxide:—



The above explanation is that suggested by Hinshelwood. There seems to be no reason, however, why the reaction should not take place as follows:—



The first of these reactions would be comparatively slow, and the second very rapid. It is the slow reaction that decides the speed of the complete change.

This reaction was first studied from the kinetic point of view by Daniels and Johnston, by measuring the pressure after various time intervals. In order to be certain that the reaction was not catalysed by the walls of the vessel (in which case it would be heterogeneous), glass wool was introduced into the reaction vessel, but no variation in the velocity constant was found. Such a variation would obviously be expected if catalysis occurred. Reactions catalysed by the walls of the vessel are frequently called "wall-reactions".

The thermal decomposition of phosphine, PH_3 , was considered for some time to be a homogeneous unimolecular reaction, but was shown by Hinshelwood and Topley to be a wall-reaction. By varying the amount of surface, the reaction was shown to be heterogeneous up to a temperature of $1,044^\circ \text{Abs.}$ at least.

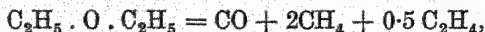
The thermolysis (thermal decomposition) of certain organic molecules seems to provide a number of first-order reactions. Thus the thermal decomposition of acetone at about 500° has been investigated by Hinshelwood and Hutchison (1926), who found it to be a homogeneous unimolecular reaction. The acetone breaks down primarily into carbon monoxide and two methyl groups, which then interact to give various hydrocarbons. The time of half-change was found to be independent of pressure over a wide pressure range. The reaction was investigated manometrically.

The thermal decomposition of propionaldehyde provides a similar first-order reaction. It gives carbon monoxide and a mixture of hydrocarbons consisting mainly of ethane and methane. At higher pressures, the time required for the completion of any definite fraction of the reaction is independent of the initial pressure, *i.e.*, of initial concentration. At lower pressures the velocity constant falls (see §214).

The thermal decomposition of dimethyl ether takes place according to the equation



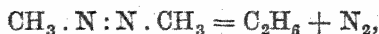
Here there is intermediate formation of formaldehyde, but this can be allowed for in the manometric determination of the rate of reaction. The reaction is first-order. A similar reaction is the action of heat on diethyl ether:—



which has also been shown to be first-order. Here, again, the constant falls at low pressures.

The racemisation of pinene in the gaseous state is a reaction which has been studied polarimetrically by Smith, and is found to obey the

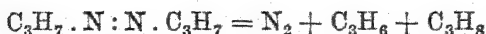
first-order law. The breakdown of azomethane, according to the equation



has also been studied, and found to be homogeneous and first-order. A similar first-order change is found in the decomposition of azoisopropane, which takes place as follows:—

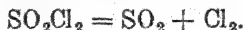


The reaction



also takes place to a small extent.

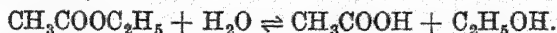
An inorganic reaction which has been studied in this connection is the decomposition of sulphuryl chloride



This reaction is peculiar in being homogeneous in vessels made of Pyrex glass, yet heterogeneous in vessels of ordinary soda-glass. There seem to be two simultaneous reactions, one homogeneous and the other heterogeneous, going on under these conditions.

207. Pseudo-unimolecular Reactions.—All the unimolecular reactions already referred to take place in the gaseous phase, and it has been pointed out how comparatively rare a truly homogeneous reaction of this kind is. A few examples of homogeneous unimolecular reactions taking place in the liquid phase are known, but here again, they are uncommon.

Many reactions appear to give a unimolecular constant, *i.e.*, they obey the equation derived above for this type of reaction, yet they are not truly unimolecular. Consider what happens in a reaction such as the hydrolysis of ethyl acetate



If a large excess of water is used in this reaction, the amount of it used up in the hydrolysis is small compared with its total mass, and consequently its active mass does not suffer greatly by the change, and can be regarded as constant. Applying the mass law,

$$v = k [\text{CH}_3 \cdot \text{COOC}_2\text{H}_5] [\text{H}_2\text{O}].$$

If $[\text{H}_2\text{O}]$ is constant,

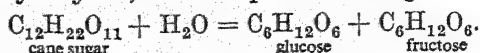
$$v = k' [\text{CH}_3 \cdot \text{COOC}_2\text{H}_5].$$

Thus, the equation is of the form of that for a unimolecular reaction, the only difference being in the value of the velocity constant k .

This is a general rule, and must be carefully borne in mind. Many bimolecular reactions may be made to appear unimolecular by taking one of the reactants in great excess.

Another example of a reaction of this kind is the rate of inversion of cane-sugar. This is brought about by dilute solutions of acids (or

alkalis), and also by enzymes, but takes place according to the equation,



It is clear that this change should be bimolecular, and not unimolecular, but in dilute solution the active mass of the water does not alter appreciably, and so the unimolecular law is obeyed. This reaction is a particularly suitable one to study, because it can be followed so easily. The reason why the reaction is called "inversion" is because the cane-sugar itself is optically active (§ 183), rotating the plane of polarisation of light to the right (dextrorotatory), whilst the resulting mixture of glucose and fructose is laevo-rotatory. The reaction can therefore be followed by means of the polarimeter, an instrument for measuring the amount of rotation of the plane of polarisation of light (§ 183). The rotation is measured at various intervals. The experimental details for carrying out this experiment are given at the end of the chapter. If the initial rotation is r_a and the rotation after a long while, r_∞ , and r_x the rotation after time t , then the amount of sugar remaining unchanged at time t is proportional to $r_x - r_\infty$.

$$\text{Hence} \quad k = \frac{1}{t} \log_e \frac{r_a - r_\infty}{r_x - r_\infty} = \frac{2.303}{t} \log_{10} \frac{r_a - r_\infty}{r_x - r_\infty}.$$

This reaction has been tested by various investigators, and the figures obtained by Lewis are given below:—

TABLE LV.—INVERSION OF CANE-SUGAR IN 0.9 N-HCl at 25° C.

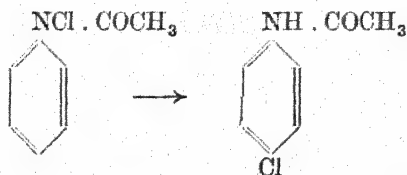
Time, mins.	Rotation, r_x	Change of Rotation, $r_x - r_\infty$	Velocity Coefficient, k
0.0	+ 24.00° (r_a)	+ 34.83°	—
7.18	21.405	32.145	0.01118
18.00	17.735	28.475	0.01117
27.05	15.00	25.74	0.01118
36.80	12.40	23.14	0.01123
46.00	10.02	20.76	0.01125
56.07	7.80	18.54	0.01125
68.02	5.455	16.155	0.01129
101.70	0.30	11.04	0.01129
∞	— 10.74	—	—

It is seen that the velocity constant calculated on the basis of the above formula is reasonably constant, and so it is inferred that the reaction obeys the unimolecular law.

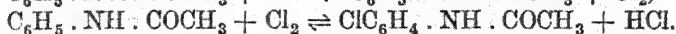
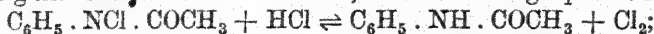
A reaction of the same type as the above is the mutarotation of glucose. When a solution of glucose is freshly prepared it is found to have a specific rotation of about 105° for the sodium D line. After standing, however, the rotation falls to about half this value, viz., 52.5°. It is quite by chance that it happens to be about one-half for

glucose, other sugars giving quite a different ratio. This phenomenon is called mutarotation, and is due to a reversible isomeric change of α - into β -glucose. This proceeds as a unimolecular reaction. It is included as a pseudo-unimolecular reaction, as it appears to be catalysed by hydrogen and hydroxyl ions (§ 378), which may take some part in the reaction.

Another reaction which gives a first order constant, and is easily studied, is the isomeric change of N-chloroacetanilide into p-chloroacetanilide.



This change takes place in the presence of hydrochloric acid which acts as a catalyst. Actually the hydrochloric acid undergoes change during the reaction and is re-formed, as the following equations show.



Thus, the change will correspond with the unimolecular formula. The reaction is very easily followed, since the N-chloroacetanilide will liberate iodine from potassium iodide. Thus, by determining the amount of standard thiosulphate required by the solution, after adding excess of potassium iodide, the amount of unchanged substance can be determined. This is done at various intervals of time. Full details for carrying out this experiment are given at the end of the chapter. Below are given some results which show that the unimolecular law is obeyed by this reaction. (See also § 54.)

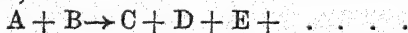
TABLE LVI.—RATE OF TRANSFORMATION OF
N-CHLOROACETANILIDE (BLANKSMA)

Time, mins.	• Titration, $\frac{a-x}{a}$	$k = \frac{1}{t} \log_e \frac{a}{a-x}$
0	49.3	—
60	35.6	0.00543
120	25.75	0.00542
180	18.5	0.00545
240	13.8	0.00531
360	7.3	0.00531
480	4.8	0.00542

The catalytic decomposition of hydrogen peroxide is a reaction of the first order as regards results, though not so in theory. The catalyst may be platinum black, or hæmase. This reaction is very easily studied. The volume of oxygen evolved at different times after the reaction has started may be determined by carrying out the reaction in a flask attached to a gas-burette. Another method is to withdraw samples of the liquid from time to time and determine the amount of hydrogen peroxide left by titration with permanganate. This experiment is described at the end of the chapter.

Why do we make a distinction between homogeneous unimolecular reactions and those which give the unimolecular constant but take place at the surface of a catalyst? Such a reaction is, for example, the decomposition of nitrous oxide at the surface of gold, or platinum. This gives the unimolecular constant. Hinshelwood and Green found that the decomposition of nitric oxide at the surface of a hot platinum wire was also unimolecular. The reason for putting these reactions in a different class is because they are just as much pseudo-unimolecular reactions as those already studied. The active mass of the reacting substance is that in the layer adsorbed on the catalyst (§ 374), and not that in the gaseous phase. The concentration in the gaseous phase is not always proportional to the concentration in the adsorbed layer. Consider the thermal decomposition of nitrous oxide, which is, under certain conditions, a wall-reaction, *i.e.*, takes place on the walls of the containing vessel, and is due to adsorption of the gas on the walls. If the adsorption is small, all the adsorbing places on the glass surface will not be covered, and the adsorption will be proportional to the pressure, and so also will the rate of reaction. In this instance the order of the reaction measured is its true order. But suppose that the pressure is greater, and the adsorption is therefore greater, and all the adsorbing places are full. Then further increase of pressure does not bring any more gas in contact with the catalyst, and the rate of the reaction ceases to be proportional to the pressure, and although the heterogeneous reaction is in reality a unimolecular reaction, it does not obey the unimolecular law. Similar considerations govern reactions of other orders.

208. **Bimolecular Reactions.**—In these reactions the concentrations of two molecular species may vary, or two molecules of the same species may disappear as a result of the reaction. The reaction may be written in the general case, as



Assume first that the initial molecular concentrations of A and B are the same, and call them a . After a time t , suppose that x gram-molecules of both A and B have been transformed into C and D. Then, according to the Law of Mass Action,

$$v = k(a - x)^2,$$

or,
$$\frac{dx}{dt} = k(a - x)^2.$$

Integrating this equation,

$$k = \frac{1}{at} \cdot \frac{x}{a - x} \quad (1)$$

Consider the more general case, where the initial concentrations of A and B are not the same, but different, and equal to a and b respectively. Let x gram-molecules be converted after time t . Applying the Law of Mass Action,

$$\frac{dx}{dt} = k(a - x)(b - x).$$

Integrating,

$$k = \frac{1}{t(a - b)} \log_e \frac{b(a - x)}{a(b - x)}.$$

It will be noticed that as the concentrations appear in the denominator as a product, and in the numerator only as a single term, the value of the constant obtained will depend upon the units in which the concentrations are expressed. This was not so in the case of unimolecular reactions.

The time for half-change is calculated in a way similar to that used for unimolecular reactions. In equation (1), put $x = \frac{1}{2}a$.

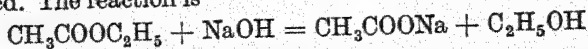
$$k = \frac{1}{t} \cdot \frac{\frac{a}{2}}{a \cdot \frac{a}{2}} = \frac{1}{at}.$$

$$\therefore t = \frac{k'}{a}.$$

It is seen that for bimolecular reactions the time for half change is not independent of the initial concentration.

Bimolecular reactions are the most common, but the number which are known to proceed in a straightforward manner is still small. A few examples of them, with their methods of investigation, will be given.

The hydrolysis of ethyl acetate is a bimolecular reaction. It has already been pointed out that this reaction may become apparently unimolecular when the quantity of the hydrolysing agent is very great. If, however, ethyl acetate is hydrolysed by means of caustic soda, and the latter is not taken in such great excess that its active mass may be assumed to be constant, it will be found that the bimolecular equation is satisfied. The reaction is



It is obvious that as the reaction proceeds, the caustic soda is progressively used up, and, by determining the amount of it left at any

given stage, the rate of the reaction may be obtained. A dilute solution of ethyl acetate is therefore mixed with an equivalent quantity of sodium hydroxide solution (in order to make use of equation (1) above and thus simplify the calculation). Measured volumes of the liquid are withdrawn at definite intervals, immediately passed into excess of standard acid to prevent any further reaction, and the excess of acid is determined by standard alkali. The concentration of sodium hydroxide found is also a measure of the amount of ethyl acetate used up. Experimental details are given at the end of the chapter. In all experiments on reaction velocity, it is necessary to maintain the reaction mixture at a definite temperature throughout, since the value of k is greatly altered by change in temperature. This is done by keeping the reacting mixture in a thermostat regulated for a suitable temperature. In this case a temperature of 25° C. is convenient.

A table of results is given below. It shows how the bimolecular constant is obtained, and that the results fail to agree with the unimolecular formula.

TABLE LVII.—HYDROLYSIS OF ETHYL ACETATE

$$a = 16.00$$

mins.	x	Unimolecular $k = \frac{1}{t} \log_e \frac{a}{a-x}$	Bimolecular $k = \frac{1}{at} \cdot \frac{x}{a-x}$
5	5.76	0.0893	0.0070
15	9.87	0.0640	0.0067
25	11.68	0.0524	0.0069
35	12.59	0.0442	0.0066
55	13.69	0.0352	0.0067

The reaction between hydrogen and iodine to form hydrogen iodide, and the reverse reaction, are both straightforward bimolecular reactions and have been exhaustively studied by Bodenstein. In the decomposition of hydrogen iodide, the gas was sealed in glass bulbs at 0° and at 760 mm. pressure, and these were then heated for a known time in a thermostat arranged for high temperatures, usually a vapour bath.

Here the calculation is somewhat more complicated, because the reaction is reversible. The two reactions, the forward and back reactions, must be considered, and if x is the fraction of the hydrogen iodide decomposed in time t , then

$$\frac{dx}{dt} = k(1-x)^2 - k' \left(\frac{x}{2} \right)^2,$$

where k is the velocity constant of the forward reaction, and k' that of the back reaction.

Let y be the fraction decomposed at equilibrium; then

$$k(1 - y)^2 = k' \left(\frac{y}{2} \right)^2,$$

$$\therefore k' = \frac{k \cdot 4(1 - y)^2}{y^2},$$

$$\therefore \frac{dx}{dt} = k(1 - x)^2 - k' \cdot \frac{4(1 - y)^2}{y^2} \cdot \frac{x^2}{4},$$

$$\therefore kt = \frac{y}{2(1 - y)} \log_e \frac{x(1 - 2y) + y}{y - x},$$

Thus, k can be calculated from a knowledge of the amount decomposed at time t , and the amount decomposed at equilibrium. A similar method can be used for the reverse reaction.

Another bimolecular reaction is the decomposition of ozone,



although the evidence in this case is rather conflicting. Hinshelwood states, however, that there seems to be no doubt that this reaction is a truly homogeneous bimolecular reaction.

The thermal decomposition of nitrous oxide, $2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$, is bimolecular in the homogeneous state, and unimolecular in the heterogeneous state. It has been investigated by Hinshelwood and Burk. They measured the rate of the reaction by observing the increase of pressure during the change. Silica vessels were employed, and the reaction was proved to be homogeneous by showing that addition of silica powder made no difference to the rate.

209. Termolecular Reactions and Reactions of a Higher Order.—

In this case the concentrations of three molecular species vary during the change, or three molecules of the same species enter into reaction. Termolecular reactions are rather rare. This is easily understood when the reaction mechanism is considered in terms of the kinetic theory. According to this theory, collision is necessary for reaction to take place. For a bimolecular reaction, two molecules have to collide, and this is quite a likely thing; hence the greater number of bimolecular reactions. In a termolecular reaction, however, three different molecules have to come together at one and the same time, and the chance of their doing this is rather small. It must depend upon the length of time two of the molecules will remain in contact. It is obvious that very few reactions of a higher order still can be expected, though a few are known.

In deriving the expression for the velocity constant of a termolecular reaction, suppose that the three reactants have the same initial con-

centration a , and that after time t an amount x of them has been transformed. Then by the Law of Mass Action

$$\frac{dx}{dt} = k(a - x)^3,$$

$$\therefore \frac{dx}{(a - x)^3} = k dt,$$

$$\therefore k = \frac{1}{t} \cdot \frac{1}{2} \left\{ \frac{1}{(a - x)^2} - \frac{1}{a^2} \right\}.$$

The time for half change is given by putting $x = \frac{a}{2}$.

$$\begin{aligned} k &= \frac{1}{t} \cdot \frac{1}{2} \left(\frac{1}{\left(\frac{a}{2}\right)^2} - \frac{1}{a^2} \right) \\ &= \frac{1}{2t} \cdot \frac{3}{a^2} = \frac{3}{2} \cdot \frac{1}{a^2 t} \\ \therefore t &= \frac{3k'}{2a^2}. \end{aligned}$$

When the initial concentrations are different the calculation is rather more complicated, and will not be given here.

The reduction of ferric chloride by stannous chloride is stated by Noyes to be a termolecular reaction. It can be written



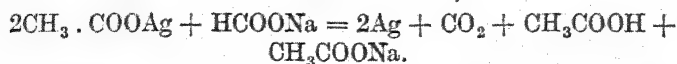
The reaction was followed by mixing equivalent solutions of stannous chloride and ferric chloride in a flask kept in a thermostat, and withdrawing quantities from time to time, the time being noted. These were run into mercuric chloride to destroy excess of stannous chloride, and then the ferrous iron was determined with dichromate. Secondary reactions take place easily, and the constancy of the velocity constant is not very satisfactory, as the following table of results shows.

TABLE LVIII.—REDUCTION OF FERRIC CHLORIDE BY STANNOUS CHLORIDE (NOYES)

t mins.	x .	$k = \frac{1}{2t} \left\{ \frac{1}{(a - x)^2} - \frac{1}{a^2} \right\}$.
1	0.01434	87
3	0.02664	87
7	0.03612	84
11	0.04102	87
40	0.05058	85

$$a = 0.0625$$

Another termolecular reaction investigated by Noyes and Cottle was the action of sodium formate on silver acetate,



210. Summary of Equations for Reactions of Various Orders.—

(1) *Unimolecular.*

$$k = \frac{1}{t} \log_e \frac{a}{a-x}.$$

Time for half change,

$$t = \frac{\log_e 2}{k}.$$

(2) *Bimolecular.*—(a) Initial concentrations of all reactants the same,

$$k = \frac{1}{at} \cdot \frac{x}{a-x}.$$

Time for half change,

$$t = \frac{k'}{a}.$$

(b) Initial concentrations of reactants different,

$$k = \frac{1}{t(a-b)} \log_e \frac{b(a-x)}{a(b-x)}.$$

(3) *Termolecular.*—Initial concentrations of reactants the same,

$$k = \frac{1}{2t} \left\{ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right\}.$$

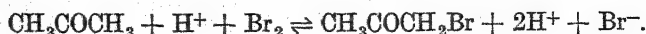
Time for half change,

$$t = \frac{3k'}{2a^2}.$$

211. Complications occurring in the Determination of the Order of a Reaction.—The number of reactions which proceed strictly according to the equations derived above is very small. The disturbing factors are chiefly: (1) the occurrence of a back reaction, (2) the occurrence of consecutive reactions, and (3) side reactions. *The effect of the back reaction* has already been considered in the thermal decomposition of hydrogen iodide, and will not again be discussed (§ 208).

Consecutive Reactions.—In some cases one reaction follows another. The equation then does not give much help in deciding the order of the reaction. The speed of such a reaction, which is made up of two or more parts, is that of the slowest reaction. Where a reaction is made up of two reactions, one of which is fast and the other slow, the kinetic treatment may not indicate the fast reaction at all. These consecutive reactions usually occur in solution, and there is often a great deal of uncertainty as to the mechanism of them.

As an example of a series of consecutive reactions, Lapworth's investigation of the bromination of acetone in the presence of hydrogen ions may be quoted. The chemical equation representing the complete change is



The velocity of this reaction is proportional to the concentration of acetone and of hydrogen ions, but is unaffected by the concentration of bromine. This can be explained as follows: the acetone, in the presence of hydrogen ions, is transformed into an enol form:—



This is a slow reaction.

The enol form rapidly adds on bromine,

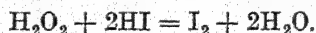


and the compound produced immediately loses hydrobromic acid,

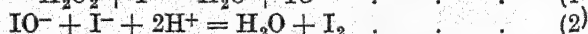
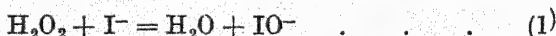


Reactions (2) and (3) are instantaneous, whereas reaction (1) is slow. The speed of the total change will be dependent largely upon the speed of the slowest link in the chain. Hence reaction (1) is the change, the speed of which governs that of the complete reaction. This explains why the concentration of the bromine does not affect the rate of the reaction.

Another example, studied by Noyes and Scott, is the reaction between hydrogen peroxide and hydriodic acid. Iodine is liberated according to the equation



This reaction proved to be bimolecular, although the equation indicated that it should be termolecular. This was explained by supposing that the mechanism was



The first reaction proceeds with measurable slowness, but the second is instantaneous. The first equation, therefore, decides the kinetics of the reaction. It may be mentioned that, as the second reaction is one of the fourth order, it, too, probably consists of a series of consecutive reactions.

Side Reactions.—When substances react, a number of independent reactions may take place, giving rise to different end products. Usually one of these reactions predominates, and is called the "main reaction", the others being called the "side reactions". It is usually possible by altering the conditions of experiment to make one or other of the side reactions assume the rôle of main reaction. In applying the Mass Law

to examples of this kind, it is necessary to take each reaction individually as if it occurred separately from the others, and connect the set up at the end, though this is, of necessity, a somewhat complicated process.

212. Methods of determining the Order of a Reaction.—The first method is to carry out the reaction and analyse the products from time to time, and then substitute the values in the various order equations (§ 210), and see which one fits the experimental data the best. This is the method most frequently used.

The second method is to determine the time required for a given fraction of the reaction to be completed, say, one-half of it. It will be seen from the equations given in §210 that the time for half change for reactions of different orders is inversely proportional to the concentration raised to the power of the order minus one. Thus, the time for half change is independent of concentration for a unimolecular reaction, whilst it is inversely proportional to the concentration for a bimolecular reaction, and inversely proportional to the square of the concentration for a termolecular reaction. Thus, if the times at which the reaction is half completed, t_1 and t_2 , are determined for respective initial concentrations of c_1 and c_2 , the equation connecting these times is

$$\frac{t_2}{t_1} = \left(\frac{c_1}{c_2}\right)^{n-1}$$

where n is the order.

As an example of this, the figures for the thermal decomposition of phosphine are given below (Hinshelwood).

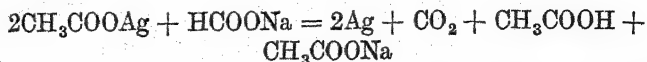
TABLE LIX.—THERMAL DECOMPOSITION OF PHOSPHINE

Initial pressure, mm.	Half-life, secs.
707	84
79	84
37.5	83

Since the times are constant for various initial pressures, the reaction must be unimolecular. It is actually a heterogeneous reaction.

The third method is known as Ostwald's Isolation Method. In this, each reactant is taken in large concentration in turn, and the order of the reaction determined by the first method. The active mass of the substance taken in great excess may be taken as constant. The sum of the orders, when each reactant is separately taken in excess, is the order of the reaction. The method may be illustrated by the reaction between

sodium formate and silver acetate, to which reference has already been made (§ 209).



When the silver acetate is taken in large excess, its active mass remains constant, and the reaction is found to be unimolecular with respect to the sodium formate. When the latter is taken in excess it is found to be bimolecular with respect to the silver acetate. Hence the reaction is termolecular.

213. The Temperature Coefficients of Chemical Reactions.—The velocity of most chemical reactions varies greatly with temperature. The ratio of the velocity constants at two temperatures separated by 10°C ., usually 25°C . and 35°C ., is called the "temperature coefficient" of the reaction. It is, as a rule, numerically between two and three. The value of the temperature coefficient is of great importance in deciding the mechanism of chemical reactions.

214. The Mechanism of Chemical Change.—Reactions take place between molecules, and, in order that there may be interaction between one molecule and another, there must be collision between them. It is highly unlikely that action could take place at a distance.

What happens when this collision takes place? Consider the two types of molecules—those in which there is an electrovalent linkage, and those in which there is a covalent linkage. It has been pointed out, in the chapter on valency (§ 76), that the bond between sodium and chlorine in sodium chloride is an electrovalent linkage. As soon as common salt is dissolved in water it ionises, and the bond is broken. It is otherwise with covalent molecules. These retain their individuality in solution. When silver nitrate and sodium chloride are brought together, silver chloride is precipitated according to the equation



The reactions $\text{NaCl} = \text{Na}^+ + \text{Cl}^-$, and $\text{AgNO}_3 = \text{Ag}^+ + \text{NO}_3^-$ have occurred before the solutions are mixed, and the reaction is $\text{Ag}^+ + \text{Cl}^- = \text{AgCl}$. The rate of this change is therefore determined by the rate at which the chlorine and silver ions can reach, and attach themselves to, the silver chloride lattice. Consequently, the reaction is almost instantaneous.

Covalent compounds do not dissociate in solution, and the breaking away of parts of such molecules involves the performance of work against linkages; and so reactions between covalent compounds are usually much slower than those between electrovalent compounds.

The simplest theory of the mechanism of chemical reactions would be that when molecules collide combination occurs, and that every collision is effective in producing combination. That this is not true is readily

down. Hence, the rate of activation and the rate of transformation are quite different.

The number of activated molecules is proportional to $e^{-E/RT}$, but only a small number of these decompose; most of them are deprived of their energy by other collisions. Hence, the chemical reaction does not disturb the number of active molecules very much. The factor $e^{-E/RT}$ is independent of pressure, and the number of reacting molecules is a definite small fraction of this, so this too will be independent of pressure. Hence, the conditions required for a unimolecular reaction are satisfied.

Let us now consider what will happen, on this theory, at low pressures. It is clear that this theory does not get over Perrin's objection as to non-activation at infinite dilution. But, consider what will happen at moderately low pressures. Here the time between the collisions will be much greater; sufficient, in fact, to allow many more of the activated molecules to go through their positions of minimum stability and break down before they collide with other molecules. Hence, as the pressure is reduced, there must be a point when the unimolecular constant begins to alter. Nearly all unimolecular reactions studied show this.

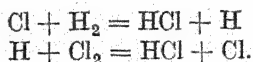
Another method of explaining unimolecular reactions, involving activation by collision, is that of Christiansen and Kramers. They state that the products of the reaction, which possess both the chemical heat of reaction and the heat of activation originally associated with the molecule before decomposition, immediately activate fresh undecomposed molecules by collision. Thus, every activated molecule which is decomposed passes on energy and ensures the production of new activated molecules. Hence, Lindemann's conclusion is reached, that the number of activated molecules is not reduced by the occurrence of the reaction, though the Christiansen-Kramers explanation appears the more satisfactory.

When the products of reaction begin to accumulate in the system, however, there will be more inert molecules with which the activated products can collide, which will merely mean a loss of activating energy. Active molecules will thus be deactivated if they collide with inactive molecules of product, or with some added molecules with which reaction does not take place, *e.g.*, some foreign gas, like hydrogen, helium or nitrogen. The theory could be tested by adding some foreign gas to the reaction mixture and seeing if the velocity of the reaction decreased. This has been done for nearly all the unimolecular reactions studied, with no effect. This favours Lindemann's theory as opposed to Christiansen-Kramers'.

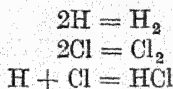
To overcome this difficulty, the latter made the assumption that the active products could only activate molecules of the reactant, and not of any inert gas, or the inactive products. Theoretically this is not such an unreasonable assumption as it appears. Nevertheless, most of the evidence is in favour of the Lindemann theory.

The way in which energy is taken up by molecules in activation has not been dealt with, but it may be stated that this process must always be governed by the quantum theory. Most available evidence shows that the vibrational motion of the molecule is of the most importance in chemical action. The quantum theory of chemical reaction regards the energy of activation as an energy "hump" which must be exceeded by the reacting molecules. The theory has been used to predict successfully the absolute value of the velocity of chemical changes in simple cases, and gives a more accurate picture than the classical theories.

215. Chain Reactions.—When a mixture of hydrogen and chlorine is exposed to light a chlorine molecule dissociates to two chlorine atoms¹ and each of these reacts with hydrogen molecules to give the series of reactions.



One chlorine atom has, therefore, produced two molecules of hydrogen chloride and another chlorine atom. This latter chlorine is now available to repeat the process. Thus a few chlorine atoms in a mixture of hydrogen and chlorine can set up a series of reactions with the above stages repeating until all the hydrogen and chlorine is used up. This process is known as a chain reaction. In this example the chain is being propagated by hydrogen and chlorine atoms; these are called the chain carriers. The removal of hydrogen and chlorine atoms by reactions such as



all break the chain. However, all these reactions involve what are called three body collision and will only take place either on the walls of the reaction vessel or in the gas phase in the presence of a third molecule. Such three body collisions are not common. The function of the third body is to remove the excess energy evolved in the reaction. Small amounts of impurities will also break these chains by combining with the chain carriers, in this case chlorine atoms.

Though chains are propagated by atoms as in the above example, free radicals can also act as chain propagators. Free radicals are radicals such as methyl, CH_3 and ethyl, C_2H_5 . They are produced by the breaking of a covalent bond, each fragment taking one electron from the bond. As a result the radicals possess an unsaturated valency and are very reactive.

For example, the thermal decomposition of acetaldehyde is supposed to involve a chain reaction carried by free radicals. The stages involved in the decomposition are firstly

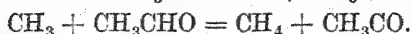
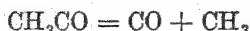


¹ See § 377 and following sections for further discussion.

These radicals then give:

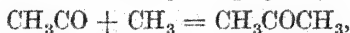


The radicals CH_3CO (stage three) and CH_3 (stage one) act as the chain carriers. Thus:



In other words the chain is being carried by the radicals CH_3 , CHO , H and CH_3CO .

The chain is broken by reactions such as



In this reaction a stationary state is reached; that is a state in which the rate of formation of chain propagating radicals is equal to the rate of their removal.

When each reacting molecule is replaced by more than one chain carrier a number of so-called branching chains are set up and there is no stationary state in the reaction. Such a chain is called non-stationary and the velocity of the reaction will increase to explosive violence. The derivation of equations to account for the kinetics of reactions in which a chain mechanism is operating is complicated and will not be discussed here.

The occurrence of free radicals is not confined to chain reactions. Free radicals such as methyl and ethyl have been prepared by heating the appropriate lead tetra-alkyl to 700°C . in a current of nitrogen at low pressure. The life-time of such radicals is very short and their presence is detected by passing them over a lead mirror. This will disappear as the radicals combine with it to reform the lead tetra-alkyl.

SUGGESTIONS FOR FURTHER READING

HINSHELWOOD, C. N. "Kinetics of Chemical Change in Gaseous Systems." (*Oxford University Press, 1947*.)

Consult the original papers mentioned in this book. They will give a valuable insight into the difficulties of this work, which cannot be gone into here. For a discussion of the Radiation Theory, see the Faraday Society discussion on "Radiation and Chemistry", *Trans. Faraday Soc.*, 1922, 546. Papers by the chief exponents of this theory—Perrin and McC. Lewis—were given. See also the Chemical Society Discussion on "The Critical Increment of Homogeneous Reactions" held on December 17th, 1931.

MOELWYN-HUGHES, E. A. "Kinetics of Reactions in Solution." (*Oxford University Press, 1947*.)

LAIDLER, K. J. "Chemical Kinetics." (*McGraw Hill, 1950*.)

CHAPTER XI

THE PHASE RULE

216. The Study of Heterogeneous Equilibria. The Phase Rule.—In the last chapter, chemical equilibrium was dealt with from the point of view of the Law of Mass Action. Although that treatment was primarily concerned with homogeneous equilibria, it was also shown that it could be made to apply to heterogeneous equilibria, *i.e.*, equilibria in reactions taking place between reactants in more than one phase (§ 203).

The Phase Rule provides another method of treatment of heterogeneous equilibria. The Rule, which enables the behaviour of a heterogeneous system to be forecast under various experimental conditions, was deduced by Willard Gibbs (1874–78). It was obtained by thermodynamical deductions, and does not involve any assumptions as to the nature of matter, and so is not dependent upon any hypothesis concerning matter. There are no exceptions to the rule, if it is applied properly. Gibbs' treatment was highly mathematical, and his paper was published in an American journal which was not very widely read, with the result that the Phase Rule was not known and accepted for some time. It was owing to its adoption by Roozeboom, van't Hoff, and Ostwald, and the examples they brought forward of its application, that it became generally known. The Phase Rule co-ordinated a number of phenomena under one law, and by its use the behaviour of previously untested systems could be forecast.

217. The Terms Involved.—The Phase Rule is stated in terms of the number of *phases* present in a system at equilibrium, the number of *components* of which the system may be made up, and the number of *degrees of freedom* which may be altered without causing an alteration in the number of phases. It is difficult to put the Rule into words, and for that reason it is best expressed mathematically by the equation

$$P + F = C + 2,$$

where P is the number of phases, C the number of components, and F the number of degrees of freedom.

It must be pointed out that the Rule only applies when equilibrium has been attained. There must be such a quantity of each phase present that when more is added the equilibrium is not altered.

It is now necessary to obtain some idea of what these terms mean. It must be emphasised that for a proper understanding of, and capacity

to apply, the Phase Rule, the meaning of the terms involved must be perfectly understood.

Phase.—A phase may be defined as any part of a system which is homogeneous throughout, and is separated by a bounding surface from other homogeneous parts of the system.

Consider ice, water, and water vapour. These are three phases of the same substance, water, and all three can exist together, as will be shown later. It is usual, however, for only two to exist side by side. Thus, if a beaker of water were to be placed in a vessel which could be evacuated, the number of phases present after evacuation (and before, for that matter, see below) is two—water, and water vapour. Consider a saturated solution of common salt, with excess of solid salt remaining over, under similar circumstances. Here the number of phases is three—the solid salt, the salt solution, and the water vapour. Each phase must, of course, be in one of the states, solid, liquid or gas. In the gaseous state there can only be one phase, no matter how many different molecular species make it up, since gases are always completely miscible. A gas mixture is always homogeneous, and thus falls within the definition of a phase. Thus, when we have a beaker of water exposed to the air, there are still only two phases present—a liquid phase, the water, and a gaseous phase, water vapour and air.

Liquids may, or may not, form a single phase. It depends on their miscibility. If a liquid is immiscible with another there will be two phases. If it is partly miscible there may be one phase, or there may be two, depending upon the concentration.

Solids are invariably regarded as separate phases, except in the instance of a solid solution. Otherwise, even though the mixture be made very intimate, the number of separate molecular species present gives the number of phases. Thus, many forms of sulphur can exist together; these are all separate phases.

It must be carefully borne in mind that the Phase Rule itself has nothing whatever to do with the amounts of the different phases present (apart from the fact that there must be sufficient of the phases to give equilibrium), but merely their number.

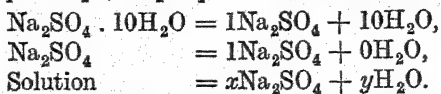
Components.—The number of components in a system is the smallest number of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.¹

It is rather more difficult to grasp the meaning of the term "component" than it is that of "phase", but some examples will make the matter clearer.

Consider an equilibrium system containing sodium sulphate and water. Such a system could include various phases—water, vapour, ice, various hydrates of sodium sulphate; but the composition of each

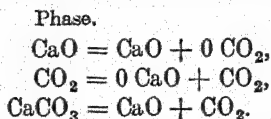
¹ Findlay "The Phase Rule and its Applications" (Longmans), p. 8.

phase can be expressed by chemical equations which involve only anhydrous sodium sulphate and water. Consider three of the possible phases— $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, Na_2SO_4 , and solution. Then

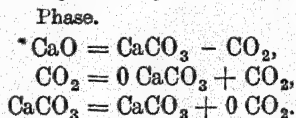


The *smallest* number of independently variable constituents by which the composition of the phases present at equilibrium can be expressed is two— Na_2SO_4 and H_2O . This is referred to as a two-component system.

In the dissociation of calcium carbonate by heat, there are three different molecular species, but the composition of each phase can be expressed in terms of any two of the molecular species. Thus, the possible phases present at equilibrium are calcium carbonate, CaCO_3 , calcium oxide, CaO , and carbon dioxide, CO_2 . If any two of the constituents are chosen, the composition of all the phases is determined. Take, for example, CaO and CO_2 for the two constituents; then,



If, now, CaCO_3 and CO_2 are chosen for the two constituents,



In both examples, the smallest number of constituents which fix the composition of the phases present at equilibrium is two, and this again is a two-component system.

In the system—sulphur and its allotropes, liquid sulphur, and sulphur vapour—the compositions of all the phases can be expressed in terms of one constituent, sulphur, and this is therefore a system of one component.

Degree of Freedom.—The number of degrees of freedom of a system is the number of factors, temperature, pressure, and concentration of the components, which may be varied without altering the number of phases present.

Pressure, temperature, and concentration are the only variables concerned in the definition of "degree of freedom" (for all ordinary purposes). Any particular phase may be able to exist under different conditions of these variables, but other variables will not enter into the question. Thus, the electrical condition of the system might be altered, but such a variable is not regarded as a "degree of freedom" from the Phase Rule point of view, because it has no specific action on the course of chemical change. It is usual, in Phase Rule deductions, to regard

capillary forces as negligible. Otherwise, an extra degree of freedom, the surface tension (or interfacial tension), would have to be introduced, for it is known that variation in this may influence the course of a chemical change, owing to difference in concentration of the substance in the surface layers (§ 360).

Suppose there is a gaseous phase only. It is known that the product of the pressure of the gas and its volume is constant, if the temperature is constant. If, then, the temperature and the pressure are fixed, the volume of the gas is fixed, and the system is completely defined. In other words, if the temperature and pressure of a gas are given, the volume (and hence the concentration, since volumes fixes it) must follow. Thus, it is necessary to fix only two of these variable factors in order completely to define the state of the system, or two may be varied without altering the number of phases present. The system therefore has two degrees of freedom.

Consider now a system made up of water in contact with its vapour. The vapour pressure will depend on temperature, but is not affected by the amount of water present. Hence, on fixing the temperature, the vapour pressure is fixed, and conversely. This, then, is a system with one degree of freedom.

218. Application of the Phase Rule to Systems of One Component.—Having defined the terms involved in the statement of the Phase Rule, we can now proceed to study a few systems by its aid.

The Water Vapour—Water—Ice Equilibrium.—In this system there is only one component, but the number of phases may be varied. If three phases—ice, water, and vapour—exist together, we have $P = 3$, $C = 1$, and the Phase Rule,

$$P + F = C + 2,$$

gives the result $F = 0$.

The system, therefore, has no degree of freedom, and is called a "non-variant" (or "invariant") system. What does it mean for a system to have no degree of freedom? Turning to the definition of degrees of freedom, it is seen that it means that none of the variables, pressure, temperature, or concentration, can be varied without one of the phases disappearing from the system. Thus, the three phases can only exist together under one condition of temperature and pressure. At the point of co-existence the temperature is $+ 0.0075^{\circ} \text{C.}$ and the pressure 4 mm.

If only two phases exist together, say ice and water, or ice and vapour, or water and vapour, the system now has one degree of freedom, and is said to be univariant. This means that one of the degrees of freedom, say temperature, may be varied without causing any alteration in the number of phases.

These facts, obtained by a consideration of the Phase Rule, may be

tested by experiment. The equilibrium between water and its vapour may be represented by its vapour pressure curve, which tells the pressure of vapour in equilibrium with water at any given temperature. This curve is the curve OA in the diagram (Fig. 120). The equilibrium between ice and vapour is similarly the vapour pressure curve of ice, and is represented by OB. The equilibrium between water and ice is expressed by the effect of pressure on the freezing point of water. Obviously the curve showing the relationship between freezing point and pressure represents the equilibrium between solid and liquid water. This is OC. It is found by experiment that these curves meet in a point O. This is called the triple point, and is obviously the point where

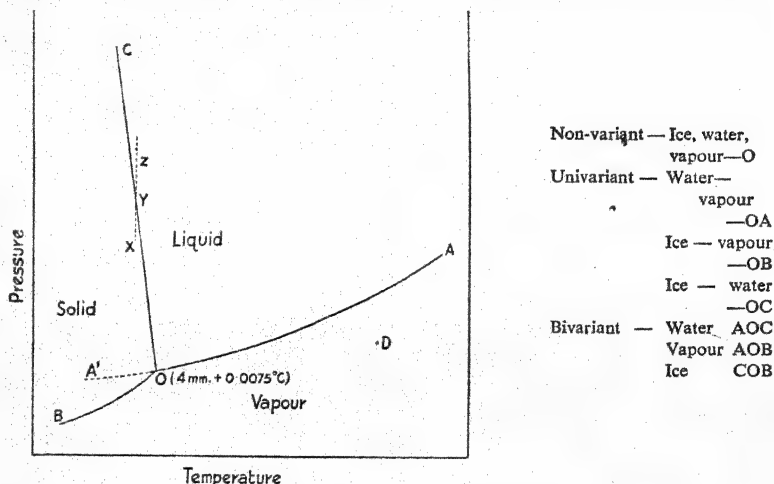


FIG. 120.—The p - t Diagram for Water (not drawn to scale).

ice, water and vapour can co-exist. Note that it is a *point*, showing that there is only one set of conditions under which it is possible for the three phases to exist together, as predicted by the Phase Rule.

The lines in this diagram represent the equilibrium conditions between two phases, and express the fact that one variable can be altered without losing a phase. Returning to the triple point, it is seen that once the conditions are moved away from that point, one phase disappears. Which one it is depends upon the direction in which we move away from the point. *Anywhere* along any of the lines, however, two phases are in equilibrium. In any of the areas bounded by the lines, one phase only is present. Thus in the area AOC liquid water only is the stable phase. In AOB water vapour only is the stable phase. If it were possible to have water at a temperature and pressure represented by the point D, it would be metastable, and once set off it would all turn into

vapour. It is thus seen that in a diagram of this kind a point represents the existence of an invariant system, a line a univariant system and an area a bivariant system. Thus, provided we keep in the area AOB, we can have vapour at any temperature and pressure. By altering one of the variables we do not alter the number of phases. It is possible to supercool water, and thus to continue its vapour pressure curve to A', but the dotted line represents a metastable state.

The curve OA ends abruptly at a point, corresponding to the critical temperature (374°C.) and pressure (218.5 atm.) of water (§ 161), beyond which there can be no distinction of the gaseous and liquid phases. The curve OB will end at 0° Abs. , and zero pressure, whilst no limit can be fixed to OC.

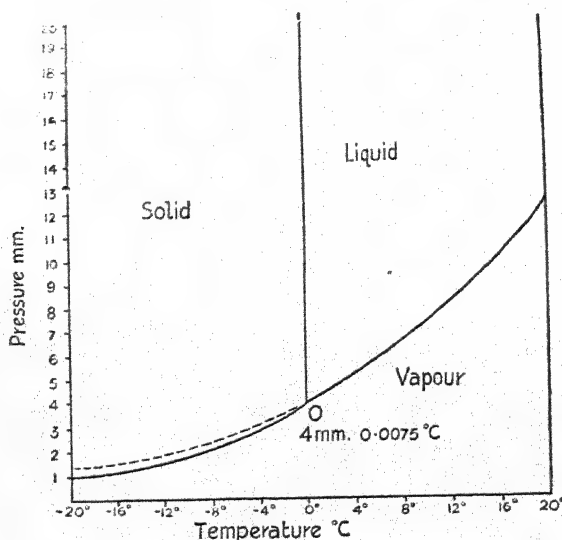


FIG. 121.— p - t Diagram for Water in the neighbourhood of the Triple Point.

The slope of the curve OC shows that ice melts with decrease of volume. This follows from the theorem of Le Chatelier (§ 199). According to this theorem, if the temperature is kept constant, and the pressure is increased, that change will take place which is accompanied by decrease in volume. The vertical line XYZ (Fig. 120) represents change of pressure at constant temperature. If the pressure is increased when the system is at the point Y, the temperature being kept constant, the new conditions are represented by Z, i.e., liquid has been formed. Hence, the melting of ice is accompanied by decrease in volume. Had the curve OC sloped the other way, Le Chatelier's theorem would have indicated an increase in volume on melting.

The diagram for water shown in Fig. 120 is not drawn to scale. Actually, the pressure differences for temperatures in the neighbourhood of the triple point O are minute. An accurate diagram for this part of the system is shown in Fig. 121, when the exaggeration in the scale of Fig. 120, just referred to, will be apparent. Also, the diagram (Fig. 120) has been very much simplified, no account being taken of the various forms of ice (no less than six), which exist at high pressures.

219. The Sulphur System.—The vapour pressure curves of the allotropes of sulphur have already been considered in connection with the study of allotropy (§ 146). The system may now be studied a little more fully. There are two solid phases which may exist permanently at equilibrium under the right conditions, the rhombic and the monoclinic forms of the element; also a liquid phase and a vapour phase. There are other solid phases capable of existence, but they are metastable, and are omitted from the present discussion. Liquid sulphur is probably colloidal in nature above about 160°C . (§ 150), and may therefore itself consist of two phases. This complication is also neglected in what follows. Consider now the four phases—rhombic, monoclinic, liquid sulphur, and sulphur vapour. Can all four exist in equilibrium? In this case there would be four phases, one component, and substituting in the Phase Rule equation

$$P + F = C + 2,$$

we should get $F = -1$. This is, of course, impossible; and so for a system consisting of a single component it is not possible to have four phases at equilibrium together.

It will be possible to have three or any less number of phases together, for then the conditions are similar to those holding for the water system. Thus, the three phases, monoclinic, liquid and vapour, could co-exist at a point, for the system would be invariant. The three phases, rhombic, liquid, and vapour, could theoretically exist together, but this can only occur in the metastable state. Two phases could exist along a line in the diagram, and one phase in an area. The vapour pressure-temperature curve is given in Fig. 122.

OB is the vapour pressure curve of rhombic sulphur, OA the vapour pressure curve of monoclinic sulphur, and AD that of the liquid. OC represents the equilibrium between monoclinic and rhombic sulphur, and is deduced from the effect of pressure on the transition point. AC is the equilibrium curve between monoclinic sulphur and liquid sulphur, i.e., the effect of pressure on the melting point of monoclinic sulphur. It will be noticed from the diagram that the curve representing the equilibrium between rhombic and monoclinic sulphur, OC, slopes away from the vertical, to the right; as already stated, this line represents the effect of pressure on the transition point between the two forms, and it is clear that the transition point is raised by the application of

pressure. By the theorem of Le Chatelier (§ 199), it follows that monoclinic sulphur is formed from rhombic with increase in volume. The curve AC also slopes away from the pressure axis very slightly, and so transition from liquid to monoclinic sulphur is accompanied by decrease in volume.

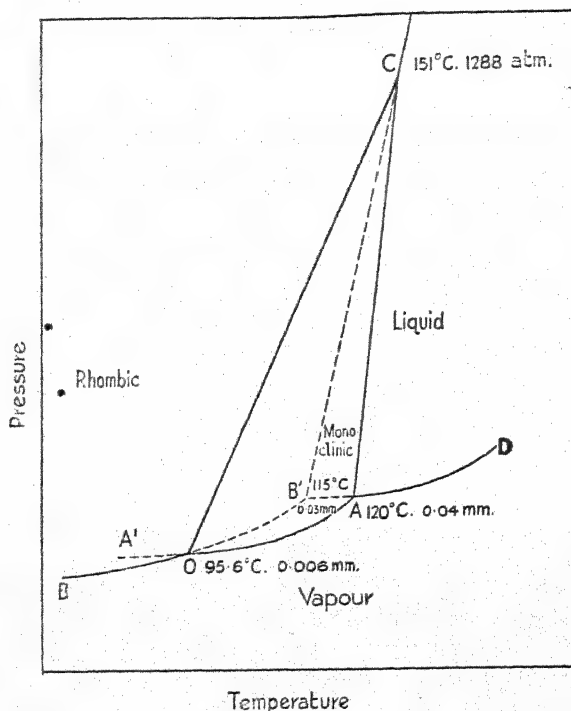


FIG. 122.—*p-t* Diagram for the Sulphur System (not drawn to scale).

At the point O there are three phases in equilibrium—rhombic, monoclinic and vapour, and if one of the variables is altered one of the phases disappears. Similarly, A is also a triple point between monoclinic, vapour, and liquid. The same remarks apply as to variation of one of the degrees of freedom. It is possible to supercool liquid sulphur down to the point B', and it is also possible to heat rhombic sulphur above the transition point along OB'. This is because the change from the one form to the other is comparatively slow. The line B'C represents the equilibrium between rhombic and liquid sulphur. The point B' is thus another triple point, but it is a metastable one, and is not frequently attained. The lines in the curve represent the equilibria between two

phases; the areas represent the existence of single substances, which can remain by themselves under any temperature and pressure enclosed by the area. Since the curves AC and OC meet at C, for which the conditions are 151° and 1,288 atmospheres, it follows that if liquid sulphur were cooled at a pressure higher than 1,288 atmospheres, rhombic sulphur would crystallise at once, no monoclinic being formed.

As with the water diagram, the scale of this curve is much exaggerated, and shows the area in the neighbourhood of the points O, A, etc., much enlarged compared with the rest of the diagram. An accurate diagram of the curves in the neighbourhood of 100° C. is given in Fig. 123. It should be pointed out that although the line OB has been drawn in

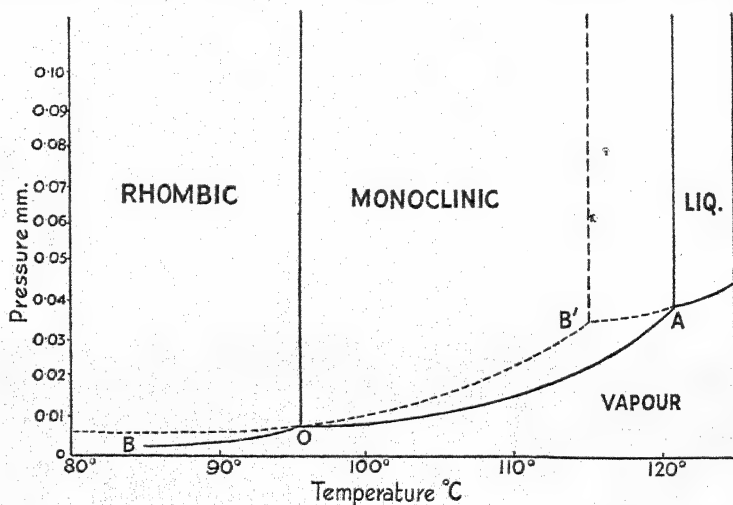


FIG. 123.— p - t Diagram for Sulphur in the neighbourhood of the Triple Points.

Fig. 122 as though it had been followed experimentally throughout its entire length; the vapour pressure of rhombic sulphur is so low that the curve has not been followed below a temperature of 85° C., as indicated in Fig. 123. The reason for drawing the curve OB in Fig. 122 is to show the general shape of it. It would follow this course if the vapour pressure could be measured.

220. Systems of Two Components.—As an example of a system of two components, we may take a metallic alloy, say an alloy of zinc and cadmium. Pressure will not have very much effect on this equilibrium, so the two variable temperature and composition only need be considered. Pressure affects equilibria the more considerably, the greater the volume changes involved. The effect of pressure will therefore be greatest in gaseous systems, and least in solid systems. If the number

of components in a system is two, it is possible to have four phases in equilibrium, but the system would be invariant. Thus

$$P + F = C + 2,$$

gives, when $P = 4$ and $C = 2$, $F = 0$.

Since the vapour pressures of solids are small, and experiments are usually carried out under atmospheric pressure, so that no gaseous phase exists, it is usual to call such a system as this a condensed system, and we can write a "reduced" phase rule

$$P + F' = C + 1,$$

the equation giving F' , the number of degrees of freedom which the system can possess in addition to the pressure. It must be remembered that an assumption has been introduced here, *viz.*, that the external pressure is large compared with the vapour pressure of the components, and so the new "reduced" Phase Rule is only approximate.

The Phase Rule diagram for alloys such as those of zinc-cadmium is given in Fig. 124. In this case there is no compound formation, and no miscibility of the components in the solid state. The curve AC represents the freezing point curve of zinc to which successive small quantities of cadmium are added. The curve BC is the freezing point curve of cadmium to which small quantities of zinc are added. C is the point at which solid zinc and solid cadmium are in equilibrium with the fused mass. At this point we have three phases, and therefore (using the reduced equation) no degrees of freedom. Hence, a *point* is found on the diagram corresponding to this condition. Along the line AC, pure zinc separates out, and is in equilibrium with the melt, so that here we have two phases only and therefore one degree of freedom, for which we should expect to have a *line* on the diagram. This is so.

The point C is called the eutectic point. If we have a fused mixture rich in zinc, and cool it, zinc will begin to separate out, and the composition of the residue will therefore be moved along the line AC until the eutectic point is reached, when the whole mass will crystallise. Similar remarks apply when an alloy rich in cadmium is taken. The dotted lines in the diagram represent the boundary conditions between the separation of crystals of one of the metals and complete solidification of the mass.

Strictly speaking, the curve given in Fig. 124 is not quite accurate. A simplification of the problem has been effected in the above treatment, which leads to a slight inaccuracy. The areas marked ACD and BCE, representing the conditions under which zinc and cadmium respectively separate from the liquid alloy, are two-phase, univariant areas (since we are dealing with a condensed system, and $P + F' = C + 1$). Univariant means here that if any *one* of the three variables, temperature, composition of solid phase, and composition of the liquid

phase, is fixed, then the other two are uniquely fixed, and cannot be varied without the disappearance of one of the phases.

The diagram (Fig. 124), on the other hand, indicates that one and the same solid phase (*viz.*, pure zinc or pure cadmium) can be in equilibrium with a continuous range of liquid compositions (all along AC or BC), *i.e.*, fixing the composition of the solid phase does *not*, according to this diagram, fix the composition of the co-existing liquid phase. As shown in the previous paragraph, this is at variance with the Phase Rule.

The strictly accurate diagram is shown in Fig. 126. Here the dotted lines represented the composition of the solid phase in equilibrium with the liquid at any given temperature. These lines deviate a little from

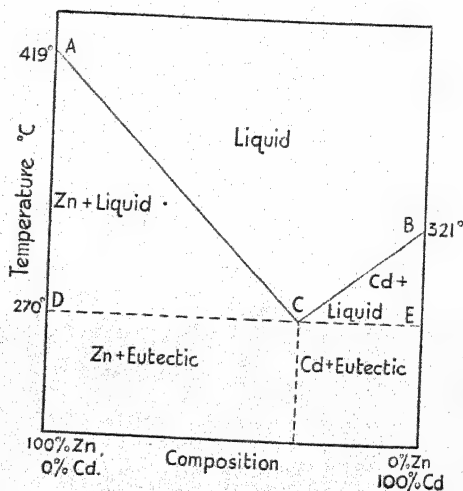


FIG. 124.—Freezing Point Diagram for Zn-Cd Alloys (simplified).

the vertical, the latter representing, of course, pure metal. In actual fact, this deviation, though theoretically necessary, may be vanishingly small, and quite unimportant for practical purposes.

An exactly similar case to this is the equilibrium between a salt and water. The eutectic point is here called the cryohydric point, and this case is dealt with in the next chapter (§ 257).

Where two substances form a solid solution, the matter is quite different. At most there can only be two phases present, liquid and solid solution, and therefore, from the "reduced" Phase Rule,

$$P + F' = C + 1,$$

F' must always be at least 1. Hence there can be no eutectic point, as in the previous case. One type of equilibrium diagram is shown

in Fig. 125. AXB is the curve indicating the equilibrium between liquid and the mixed crystals + liquid. It is the melting point curve. AYB represents the equilibrium between mixed crystals + liquid and solid, and is the freezing point curve. For a further discussion of this system, see § 264.

There is one more possibility. One or more chemical compounds may be produced. Thus, consider the case in which the two components of the system give rise to a chemical compound of definite composition. This substance will act just as if it were a foreign substance, and the freezing point curve will show two eutectics. An example is the alloy of magnesium and tin; these metals form a compound Mg_2Sn . The Phase Rule diagram is given in Fig. 127.

The eutectic B is that at which the three phases Mg, Mg_2Sn , and liquid, are present. The eutectic A is that at which Mg_2Sn , Sn and liquid are present. Along BE pure magnesium will separate out, for it is the equilibrium curve between Mg and the liquid alloy. Along AD, and also DB, the pure compound will be deposited, and along CA pure tin.

The point D is at the maximum of the curve ADB, and represents the composition of the pure compound. This follows from the fact that the

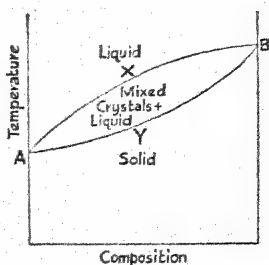


FIG. 125.—Equilibrium Curve for Mixture giving Solid Solutions.

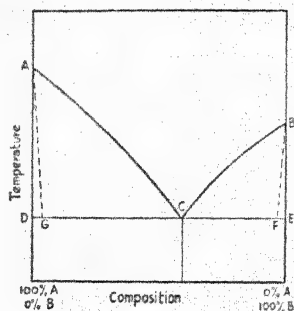


FIG. 126.—Phase Rule Diagram for Zn-Cd Alloys.

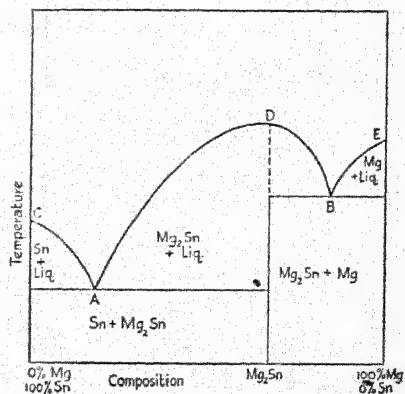


FIG. 127.—Phase Rule Diagram for Mg-Sn Alloys.

addition of a second substance to a pure compound lowers the melting point of the latter. The addition of either magnesium or tin to the compound Mg_2Sn will result in the lowering of its melting point. Hence, the maximum of the curve must represent the composition of the pure compound.

The existence of a hump in the freezing point composition curve indicates the existence of a compound. The number of humps gives the number of compounds that can be found. The curves representing the equilibrium between salt hydrates and water (solubility curves) frequently show this behaviour. In the case of the ferric chloride-water system, there are no less than four humps in the solubility curve (Fig. 163).

The vapour pressure curves of salt hydrates are interesting examples of the application of the Phase Rule. If some hydrated copper sulphate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ be placed in a tensimeter (see § 148), together with a little of the trihydrate, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, the vapour pressure of the mixture is found to remain constant so long as there is any of the pentahydrate present, but as soon as all this has been converted into the trihydrate, the vapour pressure suddenly drops until it reaches another constant level. It remains level here until all the trihydrate has been converted into the monohydrate, and then there is another sudden drop. Again the vapour pressure remains constant until all the salt has been completely dehydrated. The temperature is supposed to remain constant during these changes. These facts are represented on the diagram (Fig. 128), and are capable of a very simple explanation on the basis of the Phase Rule.

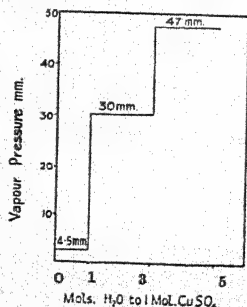


FIG. 128.—Vapour Pressure Curve of Copper Sulphate Hydrates at Constant Temperature (50°C.).

is also the water vapour. There are only two components in this system. Hence by the Phase Rule,

$$P + F = C + 2,$$

$P = 3$, $C = 2$, and hence $F = 1$. The system is univariant, but as the temperature is fixed, this one degree of freedom is removed. At constant temperature, then, the system is invariant. Hence, while there are two components, the vapour pressure must be constant. When all the pentahydrate has been converted into trihydrate, there is a sudden drop to the new dissociation pressure (§203), and the same conditions then apply. Treatment of this problem by the Law of Mass Action gives the same results (§ 203).

The phenomenon of efflorescence is closely bound up with this. The compounds $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ can only exist together at one definite pressure of water vapour. If the vapour pressure of water in the atmosphere exceeds this amount, then all the trihydrate goes into

pentahydrate; if it is less than this the pentahydrate gradually becomes transformed into the trihydrate, losing water, in making the vapour pressure of water in the atmosphere in its neighbourhood equal to the dissociation pressure. This is the phenomenon of *efflorescence*, where a hydrated salt loses its water of crystallisation and falls to a powder of some lower hydrate or the anhydrous salt.

The absorption of water by a salt, and the solution of the salt in the water absorbed is called *deliquescence*. A solid will deliquesce in moist air if the pressure of water vapour surrounding it is greater than the vapour pressure of its saturated solution. All salts would deliquesce if the vapour pressure of the water in the atmosphere were sufficiently great, but as it seldom exceeds 15 mm., and there are few salts with saturated solutions of vapour pressure lower than this, few salts actually do show this phenomenon. The vapour pressure of a saturated solution of calcium chloride is only 7.5 mm. at 20°, and so the salt is deliquescent. That of copper sulphate is 16.0 mm., and so this salt rarely deliquesces.

Many applications of the Phase Rule to two component systems are mentioned in Chapter XII.

221. Systems of Three Components.—As the number of components in a system is increased the consideration of it becomes more difficult. As examples of three-component systems there are those consisting of water and two salts with a common ion, such as $\text{KBr} + \text{NaBr} + \text{H}_2\text{O}$, $\text{NH}_4\text{NO}_3 + \text{AgNO}_3 + \text{H}_2\text{O}$, and $\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$. If new compounds are formed in a system of this type, they can only have a composition between that of two of the three components (double salts and hydrates), and thus any phase which may occur can have its composition expressed in terms of the three components. A system consisting of water and two salts without a common ion would not come into this class, since new phases might be produced by double decomposition, of which the composition could not be expressed in terms of three of the components. This would be a four-component system. If water were absent, the two salts without a common ion would form a three-component system. Another example of a three-component system is the case of a salt and water where the salt undergoes hydrolysis, *e.g.*, bismuth nitrate.

For a given number of coexisting phases, the number of degrees of freedom in a system of three components is one greater than in a system of two components. For three components, $P + F = C + 2 = 5$. The maximum number of phases is, therefore, 5, when the system is invariant ($F = 0$); and the maximum number of degrees of freedom is 4, when $P = 1$ (one gaseous phase only). When $F = 4$, the temperature, pressure and concentrations of two of the components in the single gaseous phase may be varied arbitrarily, within certain limits.

222. Graphical Representation of Systems of Three Components.—It is not always possible to represent the data for a ternary system

graphically. Very often, however, condensed systems are dealt with in which the pressure may be regarded as constant, and this simplifies matters a little. It is clear that if we have to represent the remaining

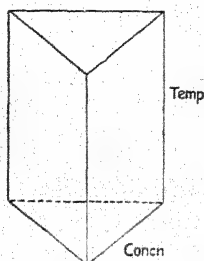


FIG. 129. — Co-ordinates for Representation of a Three-component System.

three variables, temperature and two concentrations, in a diagram, it will have to be a space diagram. This can be done by representing the composition by triangular co-ordinates, and the temperature at right angles to the composition diagram. This is shown in Fig. 129.

If the temperature is constant, the curve can be represented on a plane, being a section of the prism at the right temperature. Such diagrams are called *isothermal diagrams*, and the whole solid prism can be built up by the superposition of the isothermal diagrams. This is a good method for constructing the solid models which are required to follow these systems.

The base of the prism is taken as an equilateral triangle. The composition of each pure component is represented by a vertex. The length of the side is divided into a hundred parts. The composition of a ternary mixture is obtained by determining the distance of the point from a side measured parallel to the sides of the triangle. This method of representation is due to Roozeboom. To represent a mixture consisting of a , b , and c per cent. of the components A, B, and C respectively, one side of the triangle is divided off into a hundred parts, and a portion Bx is measured off to represent a (Fig. 130). An amount Ay is now measured off to represent b . Then the remainder, xy , must be the amount of C, as altogether the compositions must add up to 100. Through x and y lines are drawn parallel to the sides of the triangle. The point of intersection Z, is the point representing the composition of the ternary mixture. The distance of Z from the sides, measured along lines drawn parallel to the sides, obviously, from the geometry of the figure, gives the composition a , b , and c .

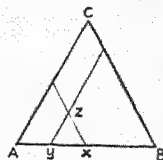


FIG. 130.

Other methods of representation have been adopted. That due to Gibbs represents the composition of the mixture by perpendicular distances of a point on the diagram from the sides.

If it is necessary to show the effect of temperature, this can only be done with a solid model, the temperature axis being vertical.

The use of triangular diagrams is shown in the study of the mutual solubility of three liquids, such as benzene, water, and acetic acid. This experiment is described at the end of this chapter.

If the compositions of two phases are represented by the points X

and Y, within the triangle, then a point P on the line joining X and Y, represents a phase consisting of a mixture of X and Y in the proportions PY to PX (Fig. 131). It follows that if the point representing the composition of a phase Z (Fig. 132) is joined to the point A, representing the pure component A, then any point R on this line represents a phase which is a mixture of A and Z in certain proportions (RZ : RA). This fact is often employed in studying saturated solutions. If the point Z in Fig. 132, represents the composition of a saturated solution, and some of the solid remaining over at the bottom of the solution is removed and analysed whilst still moist with the mother liquor, its composition will be indicated by some point such as R. The line ZR produced will cut one of the sides at some point. This point represents the composition of the solid in equilibrium with the saturated solution. It is often one of the pure components, as in the diagram we have chosen, but it need not be. In the latter case, the formation of a double-salt would be indicated. Lines such as ZR are called *tie-lines*. The analysis of a number of mixtures similar to the above give tie lines intersecting at the composition of the solid phase in equilibrium with the solution.

As one of the simplest examples of the application of the above principles, the system ammonium sulphate—ammonium chloride—

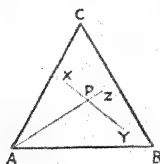


FIG. 131.

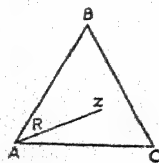


FIG. 132.

water, may be considered. It is a ternary system, since it is made up of two salts with a common ion (the ammonium ion) and water. The object is to discover whether any double-salt is formed between these two constituents. In the diagram (Fig. 133), A represents ammonium chloride, B ammonium sulphate, and C water, and it is drawn for a certain specified temperature, say 25° C. If a saturated solution of ammonium chloride is taken, its composition will be represented by a point P on AC. If, now, ammonium chloride is shaken up with ammonium sulphate solution, the composition of the saturated solution will be represented by a point, Q, inside the triangle, since it will now contain all three constituents. If the experiment is repeated with other solutions of ammonium sulphate of different concentrations, further points inside the triangle will be obtained, which all lie on the line PQR. If the damp solids as filtered from the various saturated solutions are analysed, and their compositions plotted on the triangle, it is found that the tie-lines intersect at A, showing that the solid in equilibrium with

the solutions so far considered is ammonium chloride. If, now, a saturated solution of ammonium sulphate in water is analysed, its composition may be represented by X, on BC. If ammonium sulphate is shaken up with ammonium chloride solution, and the saturated solution is analysed, its composition may be represented by a point Y. By repeating the work with ammonium chloride solutions of various concentrations, the curve RYX is obtained. Analysis of the damp solids in contact with the different saturated solutions, shows that their compositions may be represented by points on tie-lines joining the curve RYX to B. Thus the solid in equilibrium with the saturated solutions just considered is ammonium sulphate. If the tie-lines ending at R are

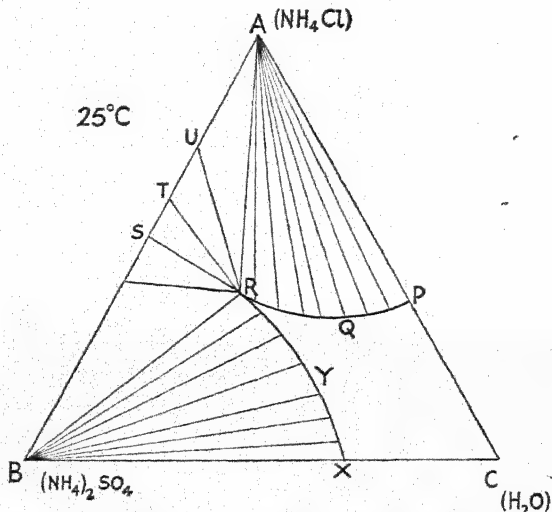


FIG. 133.—System $\text{NH}_4\text{Cl} - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$ (The diagram is schematic only, and is not drawn to scale.)

drawn, it is found that they cut the side AB at various points, A, U, T, S, B, etc. This means that the solid in equilibrium with the saturated solution represented by R is variable in composition, over the whole range $x \text{ NH}_4\text{Cl}$, $y (\text{NH}_4)_2\text{SO}_4$. There is no double-salt formation.

The interpretation of the diagram according to the Phase Rule may now be considered. There are three components—the two salts, and water at the point R, if both the salts are taken in sufficient quantity to saturate the solution. The number of phases is three—one liquid, and two solid. In a condensed system,

$$P + F' = C + 1,$$

hence, in this case, $F' = 1$. The diagram, however, is an isothermal one, so that temperature, the one remaining variable, is fixed, and the point

on the diagram is invariant. It is called an isothermally invariant point. It must be emphasised that in a three-dimensional model the point would not be invariant. The interpretation of this is, that at the temperature for which the diagram is drawn, the solution of composition R is the only one that can exist, in a stable state, in contact with both ammonium chloride and ammonium sulphate. If there is insufficient of one of these (say ammonium chloride) to saturate the solution, there are now only two phases—one liquid, and one solid (ammonium sulphate), whilst the number of components remains the same. The system is now actually bivariant, but, since temperature is fixed in the isothermal diagram, it is effectively univariant, as far as we are concerned, and the equilibrium is now represented by the line RX. In the complete model,

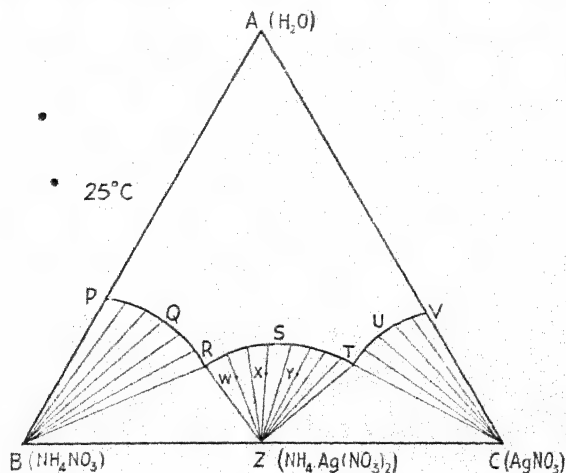


FIG. 134.—System $\text{NH}_4\text{NO}_3 - \text{AgNO}_3 - \text{H}_2\text{O}$ (schematic only).

where temperature is represented by a vertical axis, the point R, and others like it, would lie on a line (the system being univariant), and the lines RP and RX would lie on surfaces (the system being bivariant).

The above is a very simple case, in so far as there is no formation of a double-salt. In a system such as that of ammonium nitrate-silver nitrate-water, there is formation of a double-salt, the composition of which may be obtained from the diagram.

Let A (Fig. 134) represent water, B ammonium nitrate, and C silver nitrate. The point P represents a saturated solution of ammonium nitrate in water. If, now, ammonium nitrate is shaken up with a dilute solution of silver nitrate, the composition of the saturated solution is now represented by Q. Repetition of the experiment leads to points on the curve PQR. Analysis of the moist solids in contact with the various saturated solutions gives points on tie-lines connecting the curve PQR

with B, showing that the solid in equilibrium with these solutions is ammonium nitrate. If, now, the addition of silver nitrate is continued, the composition of the saturated solutions is found to lie on the line RST. The compositions of the moist solids in contact with these saturated solutions are represented by points, such as W, X, Y, which when joined up with the points representing the compositions of the saturated solutions themselves, and produced backwards, cut the BC axis at Z, which is found to correspond to the double-salt $\text{NH}_4\text{Ag}(\text{NO}_3)_2$. This salt, then, is the substance in equilibrium with saturated solutions over the composition range RST. If a saturated solution of silver nitrate is taken, its composition is represented by V. If silver nitrate is shaken

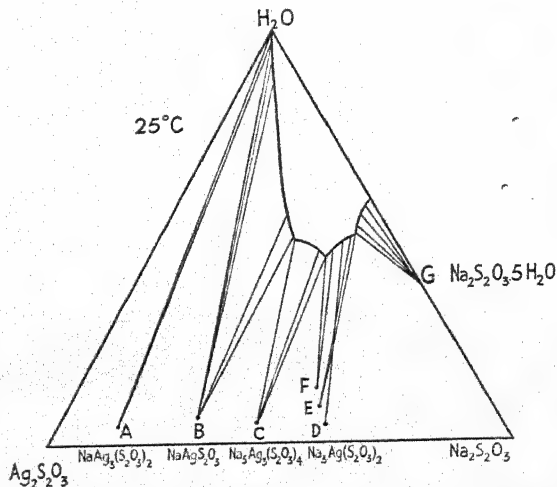


FIG. 135.—System $\text{Na}_2\text{S}_2\text{O}_3 - \text{Ag}_2\text{S}_2\text{O}_3 - \text{H}_2\text{O}$ at 25°C . (After Bassett and Lemon.)

up with ammonium nitrate solution, saturated solutions, the compositions of which are represented by points on the line TUV, are obtained. The solid in equilibrium with these solutions is silver nitrate. The two points R and T are invariant in the isothermal diagram, but actually represent univariant systems, as previously explained.

If the tie-lines happen to intersect at a point inside the triangle, the point of intersection still represents the composition of the solid in equilibrium with the saturated solution. This occurs when a hydrated double-salt is formed.

The triangular diagram may frequently be very complicated. As an example of the information that can be derived from these studies, the system $\text{Na}_2\text{S}_2\text{O}_3 - \text{Ag}_2\text{S}_2\text{O}_3 - \text{H}_2\text{O}$ may be quoted. It has been investigated by Bassett and Lemon (*J. C. S.*, 1933, 1423-1427). The

student who wishes to carry his work further is recommended to consult the original paper. A very much simplified diagram only can be given here. The form of the diagram is shown in Fig. 135.

The points A, B, C, D, E, F, G are found to represent the following salts:—

- A. $\text{NaAg}_3(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O}$.
- B. $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$.
- C. $\text{Na}_5\text{Ag}_3(\text{S}_2\text{O}_3)_4 \cdot 2\text{H}_2\text{O}$.
- D. $\text{Na}_3\text{Ag}(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O}$.
- E. $\text{Na}_3\text{Ag}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$.
- F. $\text{Na}_3\text{Ag}(\text{S}_2\text{O}_3)_3 \cdot 3\text{H}_2\text{O}$.
- G. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

All these salts are, therefore, capable of existence. In all cases, except the last, it is to be noted that the tie-lines intersect within the triangle, showing that the double-salts are hydrated.

There are many other facts that can be derived from a study of these triangular diagrams, and the student who is interested should consult one of the monographs devoted to the Phase Rule.

SUGGESTIONS FOR FURTHER READING

- FINDLAY, A. "The Phase Rule and its Applications." (*Longmans*, 1940.)
RIVETT, A. C. D. "Phase Rule." (*Oxford University Press*, 1923.)
RHODES, J. E. W. "Phase Rule Studies." (*Oxford University Press*, 1933.)

CHAPTER XII

SOLUTIONS

223. Definition of Solution.—*A solution is a perfectly homogeneous mixture.*

Solutions of all kinds may be made. Thus, solutions of gases in gases, of gases in liquids, of gases in solids, of liquids in liquids, of solids in liquids, of solids in solids, can be prepared. Each of these classes presents numerous points of interest.

A. SOLUTIONS OF GASES IN GASES

224. Application of the Phase Rule.—All gases which do not combine chemically will mix in all proportions. If a drop of bromine is placed in a large flask, the bromine vapour rises, and fills the whole vessel. In spite of the fact that it is many times heavier than air, it forms a perfect solution with air, owing to the process of diffusion.

A mixture of two gases is a system of two components, but with only one phase. Hence, according to the phase rule

$$P + F = C + 2$$

$F = 3$. The system has three degrees of freedom. This means that the temperature, concentration, and pressure can all be varied over a limited range without the risk of any new phase appearing. It must be borne in mind however, that if these variations are made sufficiently large, there is a possibility of obtaining a new phase, for one of the gases may liquefy, if the pressure and temperature are altered in the right directions, and by sufficient amounts.

225. Dalton's Law of Partial Pressures.—The pressures of gases in solutions of gases are measures of their concentrations. Indeed the usual method of measuring the concentration of a gas is by means of its pressure. A simple rule was put forward by Dalton in 1802 to express the pressure relationships in gaseous mixtures. It is known as Dalton's Law of Partial Pressures, and states that *the pressure exerted by a gaseous mixture is equal to the sum of the pressures which the constituents would exert if each occupied separately the volume of the mixture.*

The pressure that each gas would exert by itself is called its partial pressure.

This law, like all the other gas laws, is only true for perfect gases, and of course it only applies where there is no chemical combination between the gases.

There is another way of stating the law. If the gases are perfect they will obey Boyle's Law, and the volumes will be inversely proportional to the pressures. We can therefore state that—the volume occupied by a mixture of gases is equal to the sum of the volumes occupied by its constituents under the same conditions of temperature and pressure.

This is sometimes known as the Law of Additive Volumes.

226. Determination of the Partial Pressures of Gases in a Mixture.—

To test Dalton's Law all that would be necessary would be to mix two gases at known pressures and find the total pressure. If, however, we are already given a gaseous mixture and told to find the partial pressure of any gas in it, this is a more difficult matter. If a membrane can be found that will allow one gas to get through, and not the other, it is possible to carry out this experiment. Heated palladium is permeable to hydrogen, but not to any other gas, and hence the following apparatus, devised by Ramsay, can be used for determining the partial pressure of hydrogen in any mixture.

The palladium vessel, P, can be heated electrically, and is connected to a manometer. A mixture of, say, hydrogen and nitrogen, of which the partial pressures are required, is placed in the bulb, and a stream of hydrogen is passed through the outer vessel, at atmospheric pressure. When the palladium bulb is heated, it becomes permeable to hydrogen, and the pressure of hydrogen becomes the same inside and outside the vessel, i.e., equal to one atmosphere. The pressure indicated by the manometer will, however, be greater than one atmosphere, by the partial pressure of the nitrogen inside. By taking the reading of the manometer the partial pressure of the nitrogen can be obtained, and if the original pressure of the mixture were known, the partial pressure of the hydrogen originally present could be found by difference.

This experiment in itself is not of great importance, but it illustrates a method of determining partial pressures, and is very similar to experiments on osmosis in which a semi-permeable membrane is used (§ 269).

An experiment to determine the partial pressure of oxygen in air may be carried out with the apparatus described below.

The vessel A, which has a capacity of about 100 c.c., is fitted with a spiral of iron wire which can be heated electrically. It is connected by means of the two-way tap C with a manometer, B. The vessel A is first exhausted by connecting the tube D to a pump and turning the tap C. Pure dry air is then allowed to pass into the bulb, which is cooled in a

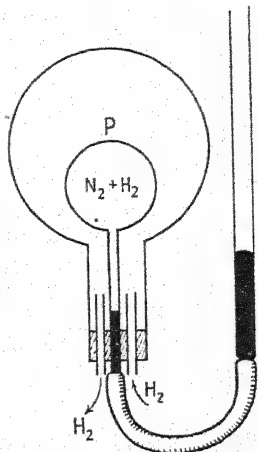


FIG. 136.—Experiment to illustrate Partial Pressures.

freezing mixture to 0°C . The tap is then turned so that the manometer is connected to the bulb, and the mercury is brought up to the mark, by raising the other limb of the manometer. The pressure of the gas is noted. The closed limb is now lowered, and the iron spiral heated. The iron combines with the oxygen, forming ferrous-ferrous oxide. After a time, the current is stopped, the air in the vessel again brought to 0°C ., and the mercury brought back to the mark. The difference in pressure

is noted. If the initial pressure was P , and the final pressure, p , the partial pressure of the oxygen was $P - p$.

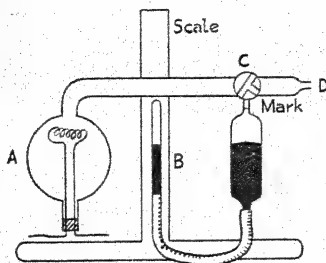


FIG. 137.—Apparatus for finding Partial Pressure of Oxygen in Air.

Where possible, it is very much easier to make use of the Law of Additive Volumes and calculate from that the partial pressure of any gas in a mixture. Thus, if a mixture of carbon dioxide and nitrogen is given, the carbon dioxide may be absorbed with caustic potash, and the decrease in volume noted.

227. Solubility of Vapours in Gases.—When a liquid A is very soluble in a liquid B, it is always found that B is very soluble in A. It is of interest to know whether a gaseous system of two components shows a similar mutual solubility between the components in each phase. Ammonia is very soluble in water. Will it attract water into the vapour phase? There is obviously an attraction between ammonia and water in the liquid state. Is there also an attraction between the two substances in the gaseous state?

There is no record of a liquid being more volatile in the presence of a gas than when it exists alone. If such a change in volatility could be found, the problem would be solved. There is, however, an obvious solution to the question. If the pressures of the two gases are determined before mixing, and again after mixing, according to Dalton's Law, the latter pressure should be equal to the total of the initial pressures. If the final pressure is less than the sum of the original pressures, it may be concluded that there is some attraction between the molecules.

MacFarlane and Wright (*J. C. S.*, 1934, 207) investigated in this way the attraction under ordinary conditions of temperature and pressure, between the vapours of methyl alcohol, ether, acetone or chloroform, and the gases carbon dioxide, ammonia, sulphur dioxide, or hydrogen chloride. It was found that these gases show considerable attraction for the vapours of the liquids in which they are soluble, though no quantitative relationship between the attraction and solubility could be deduced.

B. SOLUTIONS OF GASES IN LIQUIDS

228. Definitions.—All gases are soluble to a greater or less extent in water. Those gases which are very soluble are invariably those which form compounds with water, *e.g.*, ammonia, or dissolve to give ions, *e.g.*, hydrogen chloride.

Several definitions of the solubility of gases in liquids have been proposed. If the volume of gas dissolved in 1 c.c. of liquid is expressed at the pressure and temperature of the experiment, the figure obtained is called the *solubility*.

The *absorption coefficient* is the volume of gas in c.c.s measured at 0° C. and 760 mm. which dissolves in 1 c.c. of water.

The absorption coefficients of gases differ very much. A table showing the absorption coefficients of a number of common gases in water is given below:—

TABLE LX

Gas.	Absorption Coefficient, at 0° C.
Ammonia	1,300
Hydrogen chloride	506
Sulphur dioxide	79.8
Hydrogen sulphide	4.68
Carbon dioxide	1.713
Ethylene	0.25
Oxygen	0.049
Nitrogen	0.024

229. Determination of the Solubility of a Gas in a Liquid.—Several methods are available for determining the solubility of a gas, depending largely upon the nature of the gas; but one method of general applicability is that devised by Ostwald, using the absorptiometer.

The apparatus consists of two parts, an ordinary gas burette, G, and a gas pipette, C. The taps T and B are three-way taps, that at R, one-way. The end of the gas pipette is dipped into air-free water, the tap turned, and the pressure so adjusted by means of the burette that the vessel C becomes completely filled with water. The taps R and B are now closed, the pipette is removed from the water, and then the volume of water it contains is measured by running off into a measuring cylinder. This gives the volume of the vessel, which volume may be called v_1 . Now the pipette is filled with water as before. The tap T is

turned, to put G into communication with B and F, keeping the tap B closed. By raising H, the mercury is made to fill G up to T. Now a source of the gas of which the solubility is required is connected

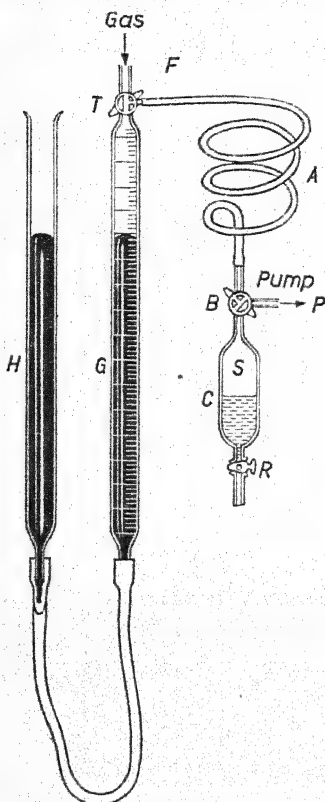


FIG. 138.—Ostwald's Absorptiometer.

to F. By opening T, connect F and B, but not G, and by opening B connect A and P, but not C. Gas now flows from F to B and out at P. Now shut B, and by the tap T connect G and A, and by lowering H fill G with gas. Keeping B closed, connect A and G, but not F, and allow to stand for about twenty minutes. It is advisable to have the tube A made of metal (lead or copper), as rubber is permeable to many gases, and also undergoes volume changes on twisting, etc. It is usually coiled into a spiral to facilitate shaking. Adjust H, and read the level of the mercury in G. This can be called h_1 . Let the height of the barometer be p , and the absolute temperature of the pipette and burette be T° .

Now put a measuring cylinder under C, and allow B and A to be connected, but not P, collecting the water that runs out when R is opened. If this volume is v_2 c.c., the volume remaining is $v_1 - v_2$ c.c.

B is now shut and the absorption vessel is shaken. B is opened and the burette reading taken. This process is repeated until a constant reading is

obtained. Let this be h_2 . The volume of gas absorbed is $h_1 - h_2 - v_2$. The volume of liquid is $v_1 - v_2$ c.c. The volume must be corrected to N.T.P. to obtain the absorption coefficient as defined above.

In this experiment it is absolutely necessary to keep the temperature of the absorption pipette constant. A slight variation may make a considerable difference to the result. It is therefore advisable to keep it in a constant temperature bath, which may or may not be at a different temperature from the gas in the burette. This temperature difference will have to be taken into account in the calculation of the result.

The absorptiometer is not a sufficiently accurate piece of apparatus for the determination of the solubility of a very soluble gas, where very small quantities of solvent would have to be used to absorb the gas

contained in so small a vessel as is there available. For this purpose, an entirely different method is used, due originally to Roscoe and Bunsen.

A bulb of the shape shown in Fig. 139 is blown from thin glass, and bent as shown. The bulb should have a capacity of from 30–50 c.c. It is first weighed empty, and then it is about two-thirds filled with the solvent to be used. It is then connected to a source of the gas, the solubility of which is required, and the gas, after drying, is passed through the solvent until saturated, the bulb being kept in a constant temperature bath. The ends of the vessel are then held in a blow-pipe, or Bunsen flame, and drawn off, the pieces removed being preserved. The apparatus, together with the pieces drawn off, is then weighed. The difference between the original weight of the dry bulb and the final weighing gives the weight of the saturated solution. It is now necessary to determine how much gas has been dissolved. The procedure depends upon the nature of the gas. Most very soluble gases are either acidic or basic. If the gas is basic, *e.g.*, ammonia, the vessel containing the saturated solution is placed in a dish containing a known volume of standard sulphuric acid, and is then broken by means of a glass rod. The ammonia solution neutralises some of the acid, which is then titrated with standard base. From the amount of acid used up by the ammonia, the quantity of ammonia present can be calculated, and hence its solubility. Similarly, if hydrogen chloride were the gas under observation, the bulb would be broken under standard base, and the amount of base left over would be determined by standard acid. Or, the vessel could be broken under water, and the hydrogen chloride directly determined.

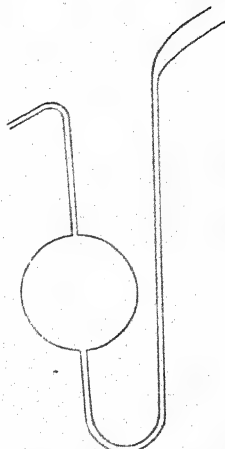


Fig. 139.—Solubility Vessel.

In very accurate work it would be necessary to make corrections for the weight of air displaced by the gas, and the weight of moist vapour filling the spaces in the bulb.

230. Nature of a Gas and its Solubility.—It has already been mentioned that the solubilities of gases vary enormously according to the nature of the gas and the solvent. Gases which give acidic or basic solutions, *i.e.*, solutions in which ions are formed, are much more soluble than others. Thus, we may compare the solubility of oxygen, which has an absorption coefficient of 0.049, with that of hydrogen chloride, of which the absorption coefficient is 506.

It is a remarkable fact that those gases which are easily liquefied are the more soluble in the usual solvents. This probably indicates miscibility of the liquefied gas with water. To illustrate this, it may be noted

that alcohol vapour is soluble in water at 90° C., and the liquid alcohol itself is completely miscible with water.

The nature of the solvent also affects solubility considerably. Thus, we may compare the solubilities of carbon monoxide and of nitrogen in various solvents. This was done by Just in 1901, and Table LXI. embodies his results. It will be noted that the ratio of the solubilities remains practically constant, so that the solubilities increase or decrease to about the same extent in the different solvents.

TABLE LXI¹

Solvent.	Solubilities (25° C.).		Ratio sol. CO sol. N ₂
	N ₂ .	CO.	
Water	0.0163	0.0240	1.47
Aniline	0.0307	0.0536	1.75
Carbon disulphide	0.0586	0.0831	1.42
Nitrobenzene	0.0626	0.0937	1.50
Benzene	0.116	0.171	1.47
Glacial acetic acid	0.119	0.171	1.44
Toluene	0.123	0.181	1.47

These remarks, of course, would not apply to gases which dissolve in some solvents with compound formation, and in others without compound formation, *e.g.*, ammonia, which dissolves in water to form ammonium hydroxide, but in benzene without compound formation.

The connection between the compressibility of the solvent and the solubility of a gas in it has been investigated. When gases dissolve, the solution usually occupies a greater volume than the original solvent, so that the solvent has to expand. It will do this against its compressibility, and so the tendency of the gas to dissolve is counterbalanced by the resistance of the solvent to expand. Experiments have shown that there is rough proportionality between the solubility of the gas and the compressibility of the solvent.

231. Solutions of Gases in Salt Solutions.—Gases are usually less soluble in salt solutions than in pure water. Carbon dioxide, however, is more soluble in a solution of sodium phosphate, and in a solution of sodium chloride, than it is in water.

Indifferent gases, such as hydrogen, oxygen and nitrogen, are always

¹ Taken from J. Newton Friend's "Physical Chemistry", Vol. I. (Griffin). The data for several other tables in this chapter have been taken from the same source.

less soluble in salt solutions, and solutions of some organic substances, than in water, the decrease being the same for all gases for a given salt concentration. It is thought that the salt may combine with some of the water, forming a hydrate, and that this water is then no longer available for the solution of the gas. If this is so, it should be possible to obtain valuable data as to the existence of hydrates, or of hydrated ions (§ 308), in solution from a study of the solubility of a gas in an aqueous solution. This has been done in the case of cane-sugar by Philip (1907). The solubility of hydrogen in cane-sugar solutions of various strengths was determined. From the decrease the degree of hydration of the cane-sugar was obtained.

TABLE LXII

Cane-sugar. Per cent.	Vol. of N ₂ absorbed at 15° C. by 1,000 gms. H ₂ O in the solution.	Mols. H ₂ O per mol. sugar.
0	18.83 c.c.	—
16.67	17.55 „	6.5
30.08	16.27 „	6.0
47.65	13.95 „	5.4

To indicate the method of calculation, the solution containing 30.08 per cent. of cane-sugar may be taken. This absorbs 16.27 c.c. of hydrogen per 1,000 gms. of water. But pure water will absorb 18.83 c.c. of hydrogen per 1,000 gms. at the temperature used. Hence, the decrease is 2.56 c.c. The fraction of the total quantity of water attached to the sugar must be $2.56/18.83$, and hence the number of water molecules attached to one molecule of cane-sugar (molecular weight 342) is

$$\frac{2.56 \times 69.92 \times 342}{18.83 \times 30.08 \times 18} = 6.00.$$

This evidence alone, of course, would be insufficient to enable us to assume that a definite hydrate of cane-sugar of the formula $C_{12}H_{22}O_{11} \cdot 6H_2O$ existed in solution, especially when it is noted that the molecular hydration decreases as the concentration of the solution increases.

The solubility of sulphur dioxide in solutions of sulphuric acid in water gives an indication of the existence of a hydrate of the formula $H_2SO_4 \cdot H_2O$, which is interesting because so many other properties of the aqueous solution of the acid show marked changes at this composition. Viscosity, density, optical properties, capillarity, specific heat and conductivity all show abrupt changes at a concentration 84.5 per cent. acid, 15.5 per cent. water, which corresponds to the monohydrate.

If the solubility of sulphur dioxide in aqueous solutions of the acid is plotted against concentration of acid, a curve is obtained similar to that shown in Fig. 140.

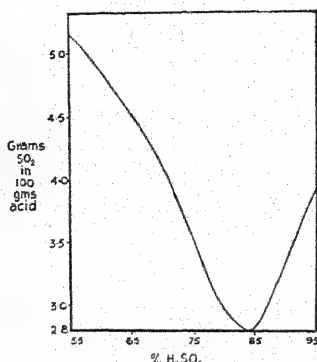


FIG. 140.—Solubility of Sulphur Dioxide in Sulphuric Acid.

Assuming that a solution of sulphuric acid in water consists of a mixture of the monohydrate and of water, the sulphur dioxide has the opportunity to dissolve in both of them. The solubility in an acid of the concentration required to give the pure monohydrate is 2.8 gms. of sulphur dioxide in 100 gms. of solution. From this, the solubility of the gas in acid of any strength can be calculated. Thus, the solubility of sulphur dioxide in sulphuric acid of strength 74.1 per cent. may be calculated. This will correspond to $(100 \times 74.1/84.5) = 87.68$ per cent. $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. The

free water present will then be $100 - 87.68 = 12.32$ per cent. Now, the solubility of sulphur dioxide in pure water is known to be 10 gms. per 100 gms. of water. Hence, the 12.32 gms. of water will dissolve 1.232 gms. of the gas, and the sulphuric acid monohydrate will dissolve $(87.68 \times 2.8)/100 = 2.455$ gms., making a total of 3.687 gms. The observed value was 3.63 gms. The following table gives the results for other concentrations, and the general agreement between the observed and calculated results gives support to the assumption made above, *viz.*, that aqueous solutions of sulphuric acid contain the monohydrate, and are, in fact, solutions of the monohydrate in water, and that the gas dissolves in both parts of the solution, the effect being additive.

TABLE LXIII.—SOLUBILITY OF SULPHUR DIOXIDE IN AQUEOUS SOLUTIONS OF SULPHURIC ACID. (Miles and Fenton.)

H_2SO_4 %	84.2	82.5	80.2	78.3	74.1	68.9	61.6	59.6
Sol. (calc.)	2.83	2.97	3.11	3.33	3.69	4.13	4.76	4.92
Sol. (obs.)	2.88	2.99	3.12	3.23	3.63	4.16	4.82	4.90

232. Effect of Temperature on Solubility.—When gases dissolve, there is usually an evolution of heat. On the basis of Le Chatelier's theorem (§ 149) it would therefore be expected that they would be less soluble at higher temperatures, and this is found to be the case. All gases except hydrogen and the inert gases, which have minima in their

solubility curves, are less soluble as the temperature is increased. This is in marked distinction from solids, of which the reverse is usually, but not always, true. Solids usually dissolve with absorption of heat, and hence they are more soluble at higher temperatures.

When a solution of a gas is heated, the gas is usually expelled. If the gas obeys Henry's Law (§233), it should all be expelled at the boiling point of the liquid, if an open vessel is used; but it is extremely difficult to get rid of the last traces of a gas dissolved in water. Even after prolonged boiling water will contain traces of air.

Certain gases cannot be expelled when their solutions are boiled, for they form constant boiling mixtures. An example of this is hydrogen chloride. If a dilute solution of this gas in water is boiled, vapour richer in water will be given off first, until the solution remaining in the vessel has reached a certain strength (20-24 per cent. at 760 mm.), when it will distil over as a whole, just as if it were a definite compound. The temperature at which this occurs is 110°C ., when the pressure is 760 mm. If the acid solution which is heated is more concentrated than this to start with, vapour richer in acid will be given off first until there remains a liquid of the above composition, which will then distil unchanged. The fact that the composition of the constant boiling mixture varies with the external pressure indicates that it is not a definite compound, although for some time it was thought to be one, especially as the composition of the mixture worked out almost exactly in agreement with the formula $\text{HCl} \cdot 10\text{H}_2\text{O}$.

The other halogen acids, and some other gases, form constant boiling mixtures which will be further discussed in connection with distillation (§ 249).

233. Henry's Law.—In the case of a solution of a gas in a liquid, two phases are present—gas and solution. There are also two components—gas and solvent; so that, according to the Phase Rule,

$$P + F = C + 2,$$

$$2 + F = 2 + 2,$$

i.e.,

$$F = 2.$$

The system is therefore bivariant. Thus, if the temperature is fixed, both pressure of gas and composition of solution can vary. If the composition is fixed, pressure and temperature may be varied.

The connection between the pressure and composition of the solution is the most advantageous to study. This relationship was first noticed by Henry (1803), and was embodied in Henry's Law, which states that *the mass of gas dissolved by a given volume of liquid at constant temperature is proportional to the pressure of the gas*. Stated algebraically

$$\frac{m}{p} = K_1 \quad \therefore \quad (1)$$

where m is the mass of gas dissolved and p the pressure.

oxygen than the original air was. If this gas is redissolved in water, and then boiled out again, it will be still richer in oxygen, and at one time it was proposed to make oxygen from the air in this way on the commercial scale. After eight absorptions, a gas containing almost 98 per cent. oxygen could be obtained.

That Henry's Law holds for other solvents besides water, providing physical solution only takes place, has been shown by numerous observers. Thus, the solution of hydrogen sulphide in aniline has been shown to obey the law closely (Bancroft and Belden, *J. Physical Chem.*, 1930, **34**, 2123) indicating that there is no compound formation in this case.

234. Experimental Verification of Henry's Law.—In the laboratory the law can easily be verified by the use of the ordinary apparatus for determining the solubility of a gas in a liquid. On altering the pressure, the volume of gas absorbed should remain constant.

The law has been verified by many investigators. The following are some of the results obtained by Morgan and Richardson¹ (1930)¹ for the solubility of oxygen.

TABLE LXIV.—SOLUBILITY OF OXYGEN IN WATER AT DIFFERENT PRESSURES

Pressure, <i>p</i> . Cms.	Mass of gas dissolved in 1 litre of water, <i>m</i> . Gms.	<i>m/p</i> .
76.0	0.0408	0.0005369
61.0	0.0325	0.0005328
41.4	0.0220	0.0005314
30.0	0.0160	0.0005333
17.5	0.0095	0.0005429

The above determinations were made at 25° C. If Henry's Law is true, the values given in the last column of the table should be constant. This is so, within the limits of experimental error. It has been shown by many others that the law holds when there is physical solution; but, when there is compound formation, association or dissociation, the law must be modified. It should be pointed out, however, that deviations from the law are encountered even with physical solution. It has also been shown that the nature of the deviations depends not only upon the

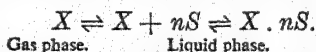
¹ For an account of the accurate determination of gaseous solubility, see the papers by Morgan and co-workers on the solubility of oxygen in various solvents in *J. Physical Chem.*, 1930, **34**, 1578, 1818, 2045, 2356.

gas, but also upon the solvent. The solubility of argon, for example in water, methyl and ethyl alcohols, pentane and other organic liquids, shows deviations from Henry's Law which are negative for water and positive for the alcohols. Such deviations cannot be accounted for by the imperfect nature of the gases. Like Boyle's Law, Henry's Law can only be true for ideal gases, and ideal solutions (i.e., those in which there is no compound formation), but in the examples now considered deviations due to the non-ideal nature of the solution are insufficient in magnitude to account for the differences observed (see § 292).

235. Deviations from Henry's Law.¹—There are three ways in which solution can take place, in addition to ordinary physical solution. There may be compound formation between the solvent and the gas; there may be association of the gas into more complex molecules; or there may be electrolytic or other dissociation of the substance (§ 297). Sometimes more than one of these possibilities is met with in the same solution.

The guiding principle to be borne in mind is that Henry's Law only holds when the *same molecular species* is considered in the two phases. Even though solution does take place in an abnormal fashion according to one or more of the above methods, we can still apply Henry's Law if we consider the molecular species present that are identical in the two phases.

(1) *Compound Formation.*—The equilibria are represented by



Actually in the solution there will be an equilibrium between the compound and the solvent and gas. This will be governed by the Law of Mass Action (§ 196).

Let C_1 = concentration of gas molecules in the gaseous phase,

C_2 = concentration of gas molecules in the liquid phase,

C_3 = concentration of solvent molecules,

C_4 = concentration of compound molecules.

By Henry's Law

$$\frac{C_1}{C_2} = K_1 \quad \dots \quad (1)$$

By the Law of Mass Action

$$\frac{C_2 \times C_3^n}{C_4} = K_2 \quad \dots \quad (2)$$

Now C_3 will be very large, and can be written as a constant. Hence,

$$\frac{C_2}{C_4} = K_3 \quad \dots \quad (3)$$

¹ This paragraph requires a knowledge of several points dealt with later in the book, and is best postponed until a second reading.

Inverting this equation, we have,

$$\frac{C_4}{C_2} = \frac{1}{K_3}$$

$$\therefore \frac{1 + K_3}{K_3} = \frac{C_4 + C_2}{C_2}$$

$$\therefore \text{from (1)} \quad \frac{C_1}{C_4 + C_2} = \frac{K_1 K_3}{1 + K_3} = K_4 \quad (4)$$

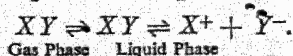
i.e., the ratio of concentration of molecules in the gas phase to the total concentration of gas molecules, both free and compound, in the liquid phase is constant. This latter is the concentration of gas in the liquid phase as determined by analysis, and so, if Henry's Law is applied to this system in the usual way, it will give an answer which is apparently correct. It is to be noted, however, that the constant calculated will have a different value from that which would be obtained if the law were applied to the true gas molecules which are dissolved, but this is the only difference. An example of a gas which follows this equation is carbon dioxide. The amount of electrolytic dissociation occurring here is so small as to be negligible.

TABLE LXV.—APPLICATION OF HENRY'S LAW TO THE SYSTEM
CARBON DIOXIDE-WATER

Temp., °C.	Pressure of Gas, <i>p</i> . Metres of Hg.	Wt. of Gas dissolved, <i>m</i> . Gms.	$K_1 = m/p$.
19.9	0.7255	38.61	52.49
	0.5245	27.24	51.94
	0.5237	27.08	51.71
	0.5231	27.28	52.13
3.2	0.5244	31.41	58.53
	0.6467	38.66	59.78
	0.6470	38.49	59.48

If, however, the compound formation is accompanied by dissociation, the case is quite different.

(2) *Dissociation*.—The equilibria now present are



Let α be the degree of dissociation, and the above symbols still retain the same significance, and let C be the total concentration in the liquid phase.

Henry's Law states,

$$\frac{C_1}{C_2} = K_1 \quad (1)$$

The Law of Mass Action states

$$\frac{(C\alpha)^2}{C(1-\alpha)} = K_2 \quad (2)$$

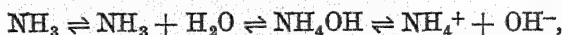
Hence,

$$\alpha = \frac{-K_2 \pm \sqrt{K_2^2 + 4K_2C}}{2C} \quad (3)$$

The negative value of the quantity under the square root sign is inadmissible.

$$\therefore K_1 = \frac{C_1}{C_2} = \frac{C_1}{C(1-\alpha)} = \frac{2C_1}{2C + K_2 - \sqrt{K_2^2 + 4K_2C}} \quad (4)$$

If this is to be tested experimentally, it is necessary to know the equilibrium constant K_2 . C_1 and C are obtained by analysis. This theory has been tested experimentally in the case of ammonia gas dissolved in water. Here the equilibria are



but the formation of the compound, NH_4OH , has no effect on the form of the equations, making a difference only in the numerical value of the constant. There is satisfactory agreement. Some of the results are shown in the accompanying table, due to Calingaert and Huggins (1923).

TABLE LXVI.—THE SYSTEM AMMONIA-WATER AT 100° C.

α .	$K = \frac{C_1}{C}$.	$1 - \alpha$.	$K_1 = \frac{C_1}{C(1-\alpha)}$.
1.256	12.92	0.987	13.1
0.633	12.67	0.981	12.9
0.148	12.13	0.963	12.6
0.0386	12.06	0.926	13.0
0.0107	11.53	0.864	13.3

The case of association can be treated in an exactly similar manner.

Where the degree of dissociation is large, the calculation can be simplified. If the concentration of single molecules in the gaseous phase is C_1 , and that in the liquid phase is C_2 , $C_1/C_2 = K$. Now suppose that dissociation takes place into two individuals. If C_3 is the concentration of each new species, by the Law of Mass Action, $C_2 = K_1 C_3^2$. Hence, the concentration of the single molecules, assuming dissociation to be large, will be proportional to the square of the concentration of the new species, which in this case is the quantity measured. Hence,

$$\frac{C_1}{K_1 C_3^2} = K$$

$$\frac{C_1}{C_3^2} = K K_1 = K_2.$$

In the case of association, let the concentration in the gas phase be C_1 , whilst the concentration in the second phase is C_2 ; and let n be the number of simple molecules in the associated complex. If the concentrations of single and associated molecules in the liquid phase are s and a

respectively, then by the Law of Mass Action $s^n = Ka$, or $\frac{s}{\sqrt[n]{a}} = C$. The

concentration of single molecules in the liquid phase is thus proportional to the n th root of the concentration of the complex molecules, which is actually measured, and Henry's Law takes the form,

$$\frac{C_1}{\sqrt[n]{a}} = K.$$

C. SOLUTIONS OF GASES IN SOLIDS

236. Types of Solution.—Gases are frequently taken up by solids, *e.g.*, palladium takes up hydrogen, and charcoal absorbs many gases.

There are four ways in which this may occur. Strictly speaking, it is not correct to term all these different ways solutions, but it will be better for our purpose if they are all considered here.

In the first place, a gas may dissolve in a solid to give a perfectly homogeneous solution in which there has been no alteration in the constitution or composition of the gas at all. This is a case of true solution, and the laws which govern this phenomenon are similar to those which govern the solution of gases in liquids.

Secondly, two or more solid solutions may be formed, and these may be only completely immiscible or partially miscible, with each other.

Thirdly, a chemical compound may be formed between the gas and the solid.

Finally, the gas may be adsorbed by the solid. By the term "adsorption" we mean taking up on the surface only. When a gas is adsorbed by a solid it forms only a surface layer. It is true that this is usually accompanied by a slow diffusion of the gas to the interior of the metal, but at first the gas is concentrated at the surface. Adsorption is an extremely important phenomenon and comes into play not only here, but also in the solution of solids in liquids, and in other cases. It largely explains the catalytic activity of powdered and finely divided metals, as will be explained in a later section (§ 374).

To decide in which of these four ways a gas has been taken up by a solid, the Phase Rule will be found especially useful.

237. True Solution.—In the case of a gas dissolving in a solid to form a true solution, Henry's Law will apply. As in the consideration of the solution of gases in liquids, the number of phases is two, and the components two. Hence, the number of degrees of freedom is also two. If the temperature is kept constant, both composition of the solution and the pressure can be altered, but one will depend upon the other. The concentration (C) and pressure (P) will be related by the equation

$$\frac{P}{C} = K.$$

If then the pressure is plotted against the composition of the solution, a straight line will be obtained, as shown in Fig. 141.

If, however, the gas changes its molecular condition when it dissolves in the solid, the relationship is, as in the case of the system, gas-liquid,

$$\frac{P}{\sqrt[n]{C}} = K$$

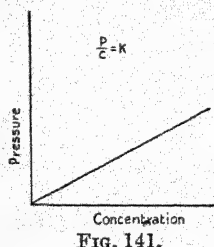
when association into molecules of n times the molecular weight takes place in the solid, and

$$\frac{P}{C^n} = K$$

when dissociation of the molecule into n parts takes place in the solid (§ 235).

238.—Formation of Solid Solutions.—It is possible for a gas to dissolve in a solid to form a solid solution, and when the concentration reaches a certain value a new solid solution may be formed which is not miscible with the first. As soon as this happens we have two solid phases, and one gas phase, making a total of three, whilst the number of components remains two. Hence, the number of degrees of freedom is one, i.e., only *one* variable can be fixed arbitrarily. If the temperature is fixed, then the pressure and compositions of the phases are automatically fixed too.

If a graph is drawn between pressure of the gas and concentration (the amount of gaseous component in the system) at constant tempera-



ture it is found to be of the form shown in Fig. 142. The portion *ab* represents the formation of the first solid solution. This is a straight line, governed by the equation $P/C = K$. There are two degrees of freedom, since we have two phases (solid and gas). One degree is lost in fixing the temperature, and so there is one left, i.e., to each concentration there is a definite pressure, giving the curve *ab*. At *b* the new solid solution makes its appearance, and there are now three phases, and only one degree of freedom in the system. As the temperature is fixed, there are no degrees of freedom left at all, and so the next part of the curve is a straight line parallel to the concentration axis. Addition of one or other component now merely alters the relative amounts of the phases, leaving their compositions and the gas pressure constant. It may be that as the concentration of gas is increased the first solid solution disappears, as it is completely converted into the second, and then there are only two phases again, and the curve would be of the form *cd*.

239. Formation of Chemical Compounds.—If a gas forms a compound with a solid, admission of large quantities of gas will fail to produce any great pressure of gas over the solid, since the dissociation pressures (§ 196) of solids are usually low at ordinary temperatures. When, however, all the solid has been converted into the compound, it may be incapable of absorbing more, or the new compound may act like the original solid and give solid solutions with the gas, or form another higher compound. If that is so, the phenomenon is governed by exactly the same considerations as those already stated, the compound being regarded for this purpose as a pure solid.

240. Adsorption.—This is the most important case of all, and the one usually met with when a gas is "taken up" by a solid. It is well known that glass and porcelain have the power of taking up moisture from the atmosphere. It is extraordinarily difficult to remove this film of moisture. To remove it completely it is necessary to heat the vessel to redness *in vacuo*. It is a surface effect, and hence finely divided solids, having a large superficial area for a given mass, will be more active in taking up gases in this way than an ordinary solid. Thus, platinum black, finely divided nickel, copper powder, animal charcoal and other kinds of charcoal are especially active as adsorbing agents.

When a gas is brought into contact with some such agent, a condition of equilibrium is set up almost immediately. A certain amount of gas is adsorbed at a given pressure, and if the pressure is altered either more gas is taken up or some is expelled. The fact that equilibrium is instantaneous points to the phenomenon as being a surface effect, for mole-

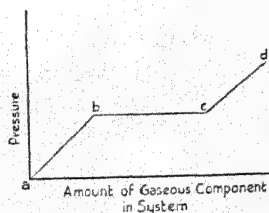


FIG. 142.

cules can diffuse only slowly through a solid. After a time, however, a further small amount of gas can be taken up, showing that there is a slow diffusion of the gas into the interior of the adsorbent.

A study of the amount of gas adsorbed by a given surface under different pressures shows that the relationship

$$\frac{x}{m} = ap^b$$

holds. In this equation, x is the weight of gas adsorbed by m gms. of solid at pressure p , a is a constant dependent upon the surface, and b a constant dependent upon the gas. b is always less than unity.

A comparison of this expression, which is called the *adsorption isotherm*, with Henry's Law shows that the two are alike in form. Henry's Law may be written in the form

$$\frac{x}{m} = ap,$$

x being the amount of gas dissolved by m gms. of liquid at a pressure p , and a being a constant. We have seen that when the pressure is raised to a power it indicates a change of molecular state of the gas in the solvent. The formula employed when dissociation takes place in the solvent is

$$\frac{C_1}{C_2^n} = K, \text{ or } \frac{x}{m} = ap^n,$$

and when association takes place

$$\frac{C_1}{\sqrt[n]{C_2}} = K, \text{ or } \frac{x}{m} = ap^{\frac{1}{n}}.$$

Hence, it might be concluded that we are dealing in this matter of adsorption with a change of molecular state of the gas when it is taken up by the solid, and, since the power b is always less than unity, the molecular weight in the adsorbed state must be less than in the gaseous state. Actually b comes out at 0.44 for ammonia, 0.39 for carbon dioxide, and 0.12 for chloroform. These values would give impossible figures for the molecular weight in the adsorbed state, so we are forced to conclude that the adsorption isotherm is an expression of an entirely different nature from Henry's Law. It is, in fact, merely empirical (§363).

241.—The Mechanism of Adsorption.—Adsorption is due to surface forces. In dealing with surface tension it was pointed out that the surface forces were due to unbalanced molecular forces. In the bulk of a liquid a molecule is surrounded on all sides by other molecules, and consequently it attracts, and is attracted, in all directions equally; but in the surface layer the molecules are subjected to fields of force which differ over their surface, and so there is the development of surface energy.

A very similar explanation can be given for adsorption. The atoms in a solid are held in position in the space lattices (§ 133) by attractive forces between neighbouring atoms. At the surface, however, they are held only partially by these forces, and so there will be a certain amount of surface energy latent. A gas molecule will be held by the atom with this extra force, and will thus be adsorbed. If the gas molecule itself possesses a certain amount of affinity for the solid, it will be held relatively firmly, and, indeed, chemical reaction may take place; but if its affinity for the metal is smaller or negligible, the only force holding the gas atom on to the metal is the unsatisfied crystal force mentioned above, and slight thermal agitation will be sufficient to remove it.

Langmuir, in accordance with this theory, believes that there are certain points on a solid surface where this additional force is centred. These points have a definite relationship to the crystal lattice. When a

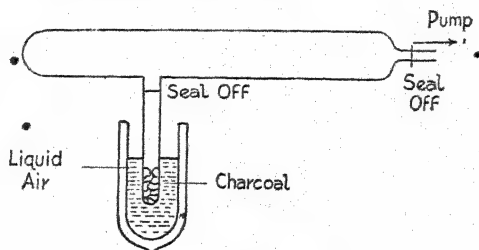


FIG. 143.

gas is admitted to a vessel containing the solid, which has been previously outgassed by heating to redness in a vacuum, it is adsorbed at these points. The pressure may not be sufficient to cause all the vacant spaces to be occupied, so that on increasing the pressure a further amount of gas is adsorbed. Ultimately, however, all the available spaces are filled, and the surface is covered with a layer of gas one molecule thick. It has been shown experimentally that in many cases of adsorption of gases the adsorbed layer is unimolecular.

When dealing with some of the gases which are most easily liquefied, or with others which are near their critical point, the adsorbed layer may be more than one molecule thick, for at this stage there are attractive forces between the molecules of the gas themselves, which will enable thicker layers to be built up. It is for this reason that the more easily liquefied gases, such as ammonia and carbon dioxide, are the more readily adsorbed by agents such as charcoal.

The fact that a gas is more easily adsorbed when it is nearing liquefaction is made use of in the high evacuation of tubes for spectroscopic work. First as much air as possible is removed from the tube (which is provided with a side-tube containing coconut charcoal, a specially active adsorbent) by means of an air-pump. Then the tube containing

the charcoal is placed in a Dewar vessel containing liquid air (Fig. 143). The charcoal adsorbs almost entirely the gas which is left, enabling a much higher vacuum to be obtained than would be possible by means of a pump alone.

The fact that finely divided metals are good catalysts in various reactions can be explained as an adsorption phenomenon, and for this reason the study of adsorption is of great importance. It will be further discussed in Chapters XVII and XVIII.

242. The Occlusion of Hydrogen by Palladium.—One of the most interesting cases of the solution of a gas in a metal is the occlusion of hydrogen by palladium. This phenomenon was first observed in 1866 by Graham, who found that palladium foil which had been previously heated to redness in a vacuum would take up 376 times its volume of hydrogen at room temperatures, 643 times at 90° – 97° C. and 526 times its volume at 245° C.

The amount of gas taken up, however, depended upon the pressure, and upon the physical state of the metal. Graham believed that the hydrogen was condensed to a sort of metal, to which he gave the name "hydrogenium", and that this formed an alloy with the palladium.

Troost and Hautefeuille in 1874 studied the effect of pressure on the occlusion. At a given temperature (say 120° C.) they found that at first the pressure increased as the concentration of gas in the metal increased, but that on further addition of hydrogen the pressure remained constant. On still further increasing the concentration of hydrogen, the pressure rose. The same thing happened at other temperatures. The results are embodied in the curves drawn in Fig. 144.

The first part of the curve, *ab*, would correspond to physical solution of the hydrogen in the metal (cf. Fig. 141). Troost and Hautefeuille considered that the straight portion, *bc*, which followed indicated the formation of a chemical compound, which, when all the palladium had been converted into it, could itself take up hydrogen, thus accounting for the renewed rise in the curve, *cd*. The palladium had taken up 600 volumes of hydrogen at the commencement of the second rise. The density of palladium is 12, so that the ratio of the weights of metal and gas in the substance formed is $12 : 600 \times 0.00009 = 12 : 0.054$. The atomic weight of palladium is 106. If the substance is a definite chemical compound its formula will be obtained by dividing these ratios by the atomic weights. The values $2.03 : 1$ are obtained, which would make the compound Pd_2H . As will be seen below, it is a mere coincidence that this is a simple ratio.

However, simply because the pressure remains constant whilst the composition varies, it cannot be argued that a compound is present. It is equally possible, as Hoitsema showed, to have two non-miscible solid solutions. We have already seen that this would give a curve of the nature required (§ 238).

It is necessary to find some way of distinguishing the two cases, so that it may be known definitely whether it is a matter of formation of a compound, or two non-miscible solid solutions. This can be done from a study of the pressure-composition curves for different temperatures. If a chemical compound is present, the pressure remains constant whilst the metal takes up more and more hydrogen until all the metal is converted into compound, after which it again rises. The concentration at which the second rise begins should be the same at all temperatures

unless different compounds are formed at different temperatures. There are only certain possibilities of this, and it must be assumed that one compound would be stable above a certain temperature, and another below it, in which case the concentration at which the second rise begins should be constant up to a certain temperature, and then suddenly take up another definite value.

If two non-miscible solid solutions are present, the concentration at which the second rise begins, i.e., the concentration at which the solutions become completely miscible, and therefore exist as one phase, will vary con-

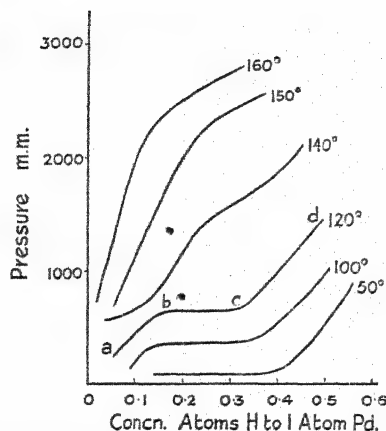


FIG. 144.—Relationship between Pressure and Concentration in the Palladium-hydrogen System.

tinuously with temperature. A glance at the curves in Fig. 144 will show that this second case is correct, and that we are dealing with two non-miscible solid solutions.

A good deal of work has been done to discover more about these solid solutions, and the conclusion has been drawn that they are in effect a solution on the surface, and a solution in the interior of the metal. The latter does not appear to be homogeneously distributed through the metal. The surface layer can be removed fairly easily by pumping, but it is much more difficult to remove the hydrogen in the interior. X-ray analysis (§ 134) of the palladium which has adsorbed hydrogen fails to show any change of structure at the beginning of the portion of the curve *bc*. A change would be expected if compound formation occurred. They do indicate, however, that there are two immiscible solid solutions, as shown by the Phase Rule treatment.

D. SOLUTIONS OF LIQUIDS IN LIQUIDS

243. General.—It was a tenet of the alchemists that *similia similibus solvuntur* (like is dissolved by like), and this appears to be generally true. Thus, water will dissolve alcohol to any extent, but will not mix with mercury. Mercury, on the other hand, will dissolve metals. Benzene will not dissolve water, but will dissolve hydrocarbons.

This generalisation has received some theoretical explanation from the electronic theory. It is found that liquids tend to fall into two classes, water and the hydrocarbons being the extreme members of each class. Liquids of the water class dissolve in each other, but as a rule will not mix with those of the hydrocarbon class. The liquids of the water class are all ionising solvents, they have higher dielectric constants than the other liquids (a property which makes them ionising solvents), they tend to polymerise in solution, and in the pure liquid state, and they have abnormally high boiling points. The liquids of the water class are termed "abnormal", whilst those of the hydrocarbon class are "normal". Sometimes the terms "polar" and "non-polar" respectively, are met with to indicate these classes of liquid; but these terms are strictly speaking incorrect, and should be avoided. Generally, associated substances are co-ordinated compounds (§ 75).

All non-associated liquids are completely miscible with each other, and all the extreme members of the associated class, *e.g.*, water and the lower alcohols, are completely miscible. If, however, we bring together a liquid of one class and one of the other, a solution will not usually be formed. Since there is this difference between molecules of the different classes, it is clear that the deciding factor is the nature of the electric fields of the molecules. In associated molecules there must be electrical forces which tend to keep the molecules together, and these give rise to an internal pressure. In normal molecules there is a very weak external field, so that if a normal substance is mixed with an associated one there will be a tendency for the two types to separate, and solution will not occur. The associated molecules will tend to remain as such and not be broken into by the normal molecules.

244. The System Phenol-Water.—If phenol is mixed with water, two liquids are produced, one a solution of phenol in water, and the other a solution of water in phenol. These two form separate layers. Now at any given temperature the composition of these layers is fixed. On warming, the amount of water in the phenol phase increases, and the amount of phenol in the water phase increases, until at a certain temperature the composition of both layers becomes the same. Then, of course, there will be complete miscibility; there will be no separation of the liquid into two layers. The system was studied by Rothmund in 1898, and the following data are due to him. They are plotted in the curve shown in Fig. 145.

TABLE LXVII.—THE SYSTEM PHENOL-WATER (Rothmund)

Temperature, °C.	10	20	30	40	50	55	60	65	68.4
Wt. per cent. phenol in aqueous phase	7.5	8.5	8.7	9.7	12.0	14.2	17.5	22.7	36.1
Wt. per cent. phenol in phenol phase	—	72.2	69.9	66.8	62.7	60.0	56.2	49.7	36.1

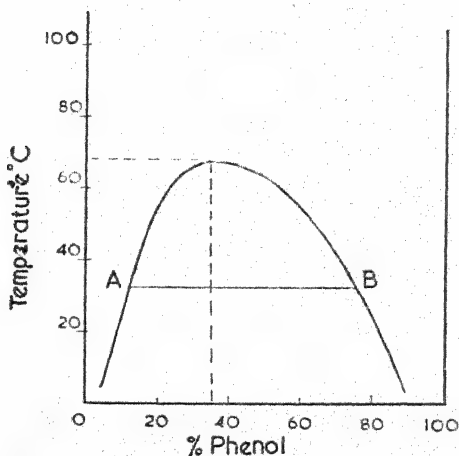


FIG. 145.—Solubility of Phenol in Water and of Water in Phenol.

The temperature at which the two phases disappear and one takes their place is called the *critical solution temperature*, and sometimes the *consolute temperature*. Since it is possible in some systems (§ 247) to have a lower temperature of a similar nature, it is also frequently called the *upper critical solution temperature*.

The solubility curve drawn in Fig. 145 is parabolic in shape (approximately), but no general formula has been derived by means of which this curve can be represented to cover all cases. Its shape, and the nature of the phenomenon with which it has to deal, recall the method of Cailletet and Mathias for determining critical volume (§ 161). At any definite temperature, the compositions of the two layers will be represented on opposite branches of the parabola. The line joining them, e.g., AB in Fig. 145, is called a *tie-line*, and the two solutions are said to be *conjugate*.

The critical solution temperature is affected very much by the presence of impurities, and may be used as a criterion of purity. For

phenol, the effect of the addition of small quantities of benzene, naphthalene and pyridine is to raise the critical solution temperature. The criticism has been made that Rothmund's value of the critical solution temperature of phenol is too high owing to the phenol used being not quite pure. According to Dolique (*Comptes rendus*, 1932, **194**, 289), the critical solution temperature of the purest phenol is $66.5 \pm 0.1^\circ \text{C}$., and the concentration at this temperature is 34.0 per cent.

245. The System Triethylamine-Water. — Here the reverse behaviour is encountered. Below 18.5°C . the two liquids are completely miscible, but above it they form two distinct layers. This system was studied by Rothmund, whose figures are given below, and are plotted in Fig. 146. Nearly all the substances which show this behaviour with water are amines, and they are not easy to obtain in a state of purity. As impurities have a considerable effect on the critical solution temperature (§ 244), it is a difficult matter to obtain accurate results in this work.

TABLE LXVIII.—THE SYSTEM TRIETHYLAMINE-WATER

Temperature, $^\circ \text{C}$.	70	50	30	25	20	18.5
Wt. per cent. amine in aqueous phase	1.6	2.9	5.6	7.3	15.5	c. 30
Wt. per cent. amine in amine phase	—	—	96	95.5	73	c. 30

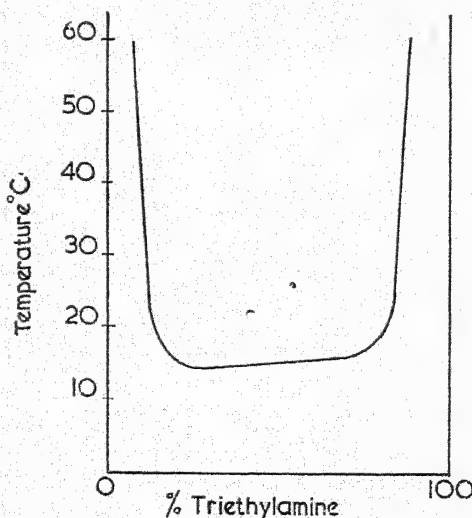


FIG. 146.—Solubility of Triethylamine in Water, and of Water in Triethylamine.

246. The System Nicotine-Water.—In this case we have a closed solubility curve. There are two critical solution temperatures—an upper and a lower. The figures obtained by Hudson (1903), and confirmed by Tsakalotos (1909) are given below, together with the graph.

TABLE LXIX.—THE SYSTEM NICOTINE-WATER

Per cent. nicotine by wt.	6.8	7.8	10.0	14.8	32.2	49.0	68.8	80.2	82.0
Lower Temperature, °C.	94	89	75	65	61	64	72	87	129
Upper Temperature, °C.	95	155	—	200	210	205	190	170	130

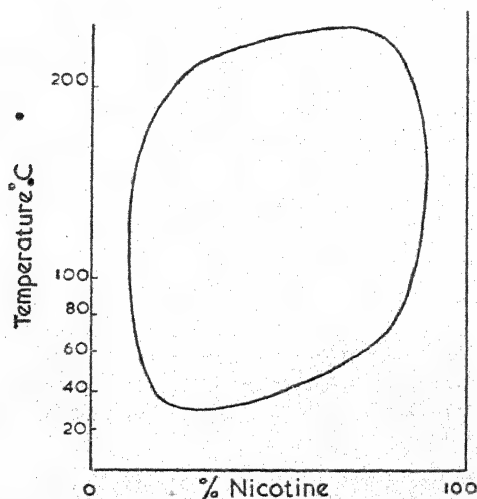


FIG. 147.—Solubility of Nicotine in Water and of Water in Nicotine.

It was found by Tsakalotos that the composition for the two critical points (60.8° C. and 208° C.) is the same. Between these temperatures two layers are obtained, but outside them there is complete miscibility.

It is interesting to note the effect of pressure on this system. Application of pressure raises the lower, and decreases the higher critical solution temperature, so that the area of the closed ring gets smaller and smaller, until finally it becomes a point, and the liquids are completely miscible over the whole range of temperature.

247. Experimental Methods of studying Mutual Solubility.—The simplest method is that used by Alexejew. Known amounts of the two liquids are introduced into tubes which are then sealed and placed in a water-bath, of which the temperature is gradually increased. The temperature at which the two layers disappear in the tubes is noted.

The tubes must be shaken frequently during the experiment. In this way a series of points on the mutual solubility curve is obtained.

Another method is to take amounts of the liquids and shake them together in a tube placed in a thermostat. When equilibrium has been attained, known volumes of each layer are analysed. This method is not easily carried out, as in some cases the analysis is difficult.

A thermostatic method devised by Hill (1923) is of interest. Different amounts of the two components are weighed into each of two vessels, and the volumes produced after equilibrium has been reached at a fixed temperature are measured. Graduated cylinders may be used for this purpose. Let m_1 and m_2 be the weights of the first component used in the two experiments, and c its concentration in grams per c.c. at equilibrium in the upper phase, and d its concentration in the lower phase. If the volumes of the upper phase are v and v_1 and of the lower w and w_1 ,

$$cv + dw = m.$$

$$cv_1 + dw_1 = m_1.$$

If these equations are solved for c and d , the concentration of the first component in each phase is determined. Similar equations are used for the second component. Adding the amount of each component present in a given phase, we have the weight per c.c., or the density, and the percentage composition by weight is obtained.

248. The Vapour Pressures of Solutions of Liquids in Liquids.—It is necessary to deal separately with the three types of solution: (a) components completely miscible, *e.g.*, alcohol and water; (b) components partially miscible, *e.g.*, ether and water; (c) components practically immiscible, *e.g.*, nitrobenzene and water. The liquids are not absolutely immiscible, but there are always two liquid phases over ordinary concentration ranges.

249. Components Completely Miscible.—Applying the Phase Rule to this case, we have two components and two phases, so that the system is bivariant. This means that if the temperature is fixed the other remaining degrees of freedom, *i.e.*, pressure and composition, must vary together. Thus a mixture of any given composition will have a fixed and definite vapour pressure at a given temperature.

If the vapour pressure of a liquid mixture is plotted against the composition, the curve obtained will be one of three types which are shown in Fig. 148.

(a) In the first case the vapour pressure curve is a straight line. The two dotted lines represent the partial pressures of the components. These are both straight lines and indicate that both components are ideal liquids, obeying Raoult's Vapour Pressure Law (§ 276), which states that the relative lowering of the vapour pressure of a solution is equal to the ratio of the number of molecules of solute and of solvent in the

solution. Such liquids are those drawn from the normal class, and which do not form compounds with each other, or cause polymerisation or dissociation.

Examples would be mixtures of benzene and toluene, and benzene and hexane. The total vapour pressure of the liquid will be the sum of the partial pressures of the separate vapours and is given by the line FD.

Consider a liquid mixture of some definite composition. The vapour from such a mixture will contain each constituent in the proportion of its partial pressure. Therefore the proportion of more volatile con-

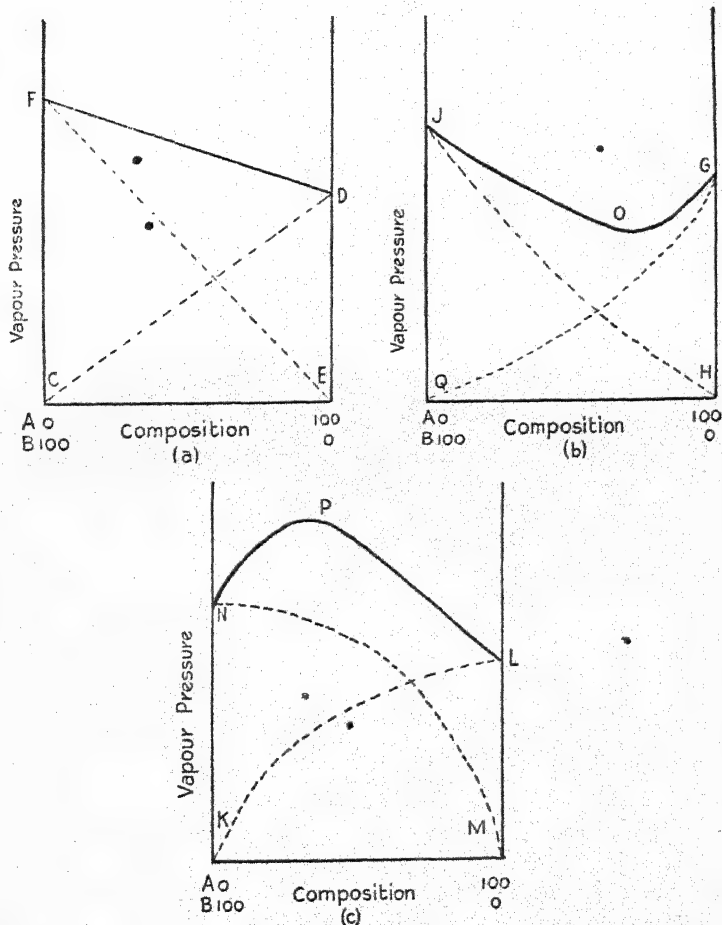


FIG. 148.—Types of Vapour Pressure-Composition Curves for Completely Miscible Liquids.

stituent will be greater in the vapour than it is in liquid with which it is in equilibrium. Suppose the vapour is removed and condensed in a separate vessel; the condensate will contain a greater proportion of the more volatile component than did the original liquid. The residual liquid will contain a greater fraction of the less volatile component than did the original liquid. This process of distillation (i.e., vapourisation and condensation) can be repeated; it enables a separation of the two components to be effected, and this is what happens in fractional distillation. This process, however, will be fully dealt with in the next section.

If the lines CD and EF were slightly curved, they would give when added a total vapour pressure curve which did not possess any definite maximum or minimum, and the same considerations would apply.

(b) In the second case the total vapour pressure curve exhibits a minimum, and this can be made up of two partial pressure curves which are concave upwards, or one straight line and one concave curve. The composition of the mixture with minimum vapour pressure is defined by the point O in the Fig. 148 (b). This mixture has the maximum boiling point: all other mixtures of A and B have lower boiling points. Further at the point O the vapour and liquid in equilibrium have the same composition and hence the composition of the mixture O is not changed by distilling it.

Examples of this behaviour are furnished by the common acids. Sulphuric acid and water form a constant boiling mixture, boiling at 338°C ., and containing 98.7 per cent. of the acid. Hydrochloric acid forms a constant boiling mixture distilling at 110°C . and containing 20.24 per cent. of the acid (§ 232).

(c) Here the mixture gives a maximum in the total vapour pressure curve. The mixture which has the maximum vapour pressure will obviously boil at a lower temperature than any other mixture. Alcohol and water and pyridine and water are examples of systems with this type of behaviour. As will be shown in the next section systems which involve maximum or minimum vapour pressure mixtures cannot be separated into their components by distillation.

250. Distillation.—It has already been stated that only one type of completely miscible mixture can be separated into its components by fractional distillation, and this is the type which gives a vapour pressure curve possessing neither a maximum nor a minimum. It is not, however, the vapour pressure-composition curve that is of so much interest for our present purpose, but the temperature-composition curve. This will, of course, be dependent upon the vapour pressure curve, but will not have the same form. If we plot the boiling point of a liquid mixture of this type against its composition we have a graph of the form XDY in Fig. 149.

The composition of the vapour in equilibrium with the liquid at the

boiling point is not the same as the composition of the liquid. It will contain more of the more volatile component. The curve XGY represents the variation with temperature of composition of the vapour in equilibrium with liquid.

Suppose we take a liquid containing about 60 per cent. A (point E on Fig. 149), and heat it until it boils at a temperature F. The composition of the vapour in equilibrium with the liquid at this temperature is the point G on FD, where it cuts the vapour curve. On cooling this vapour, the composition of the distillate is H, which is obviously richer in B than the original liquid, since B is the more volatile liquid, having a lower boiling point. If the process is repeated, the temperature at which the distillate boils is J, and the vapour in equilibrium with it has a composition L, very closely pure B. In this way a mixture of A and B can be separated into its components.

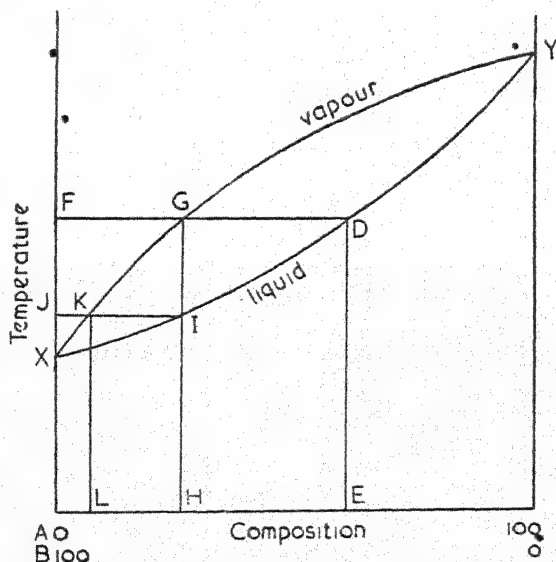


Fig. 149.—Temperature-Composition or Boiling-point Curves.

We will now consider the distillation of a mixture which has a vapour pressure curve with a minimum. The temperature composition curve of this mixture is Fig. 150(a). At the point M (corresponding to O, Fig. 148(b)) the mixture has a maximum boiling point and the liquid and vapour in equilibrium have the same composition. Hence if a mixture of composition M is vapourised and then condensed, the distillate will have the same composition as the original liquid. A mixture which distils without changing its composition is called an azeotropic mixture.

The vapour from a mixture of composition C (a point on the curve

between M and 100 per cent B) will have its composition defined by the corresponding point D on the vapour curve. Comparing the vapour with the liquid it can be seen that the vapour contains more of the more volatile component B than the liquid. This means that the distillate from the liquid is enriched in B while the residue will be enriched in A. The boiling point of the mixture rises. As the process is continued the residue will gradually approach the composition M. By taking fractions from the mixture and by a series of redistillations we can eventually obtain a distillate of pure B and a residue of the azeotropic mixture M. Further distillation of this latter will not enable us to obtain a separation into A and B as the mixture M distills without change in composition. Thus we can by a series of distillations separate the mixture into B and the azeotropic mixture. In a similar manner we can separate a mixture of composition E in (Fig. 150(a)) into A and the azeotropic mixture. We can therefore conclude that systems which involve boiling-point curves of the type in Fig. 150 (a) can be separated by distillation into the azeotropic mixture and the component which is in excess in the original mixture of that required by the azeotropic mixture.

The temperature-composition curves of systems which involve a maximum vapour pressure are shown in Fig. 150 (b). In this curve there is an azeotropic mixture defined by the composition M. This mixture has a boiling point lower than any other mixture of the components A and B. If a mixture of composition C (which can be any point between M and 100 per cent. B) is distilled then the vapour will contain more of A than did the original mixture. The residue will be

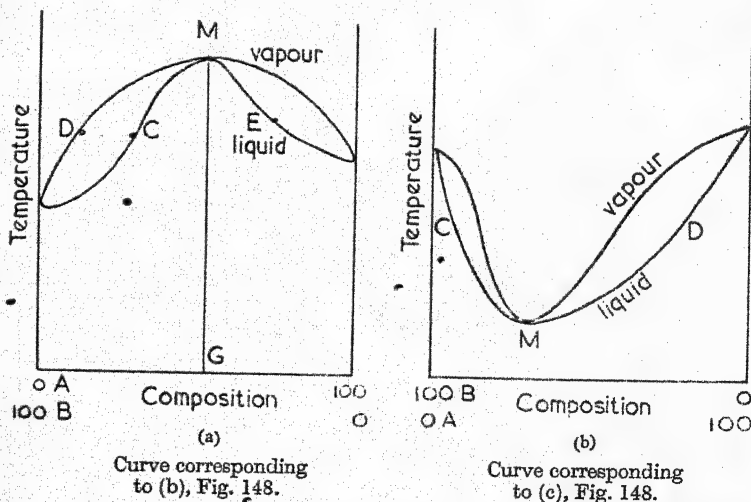
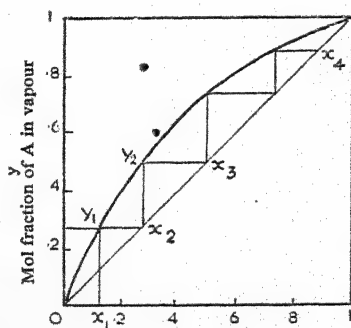


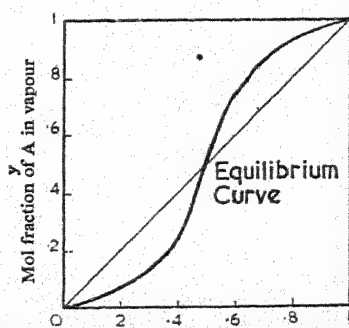
Fig. 150.—Curves showing Composition of Vapour and Liquid at different Temperatures.

enriched in B. If we take fractions from the mixture and redistil these we will eventually obtain a distillate of composition M and a residue of pure B. In the same way distillation of a mixture of composition D will lead to an eventual residue of pure A and a distillate of the azeotropic mixture.

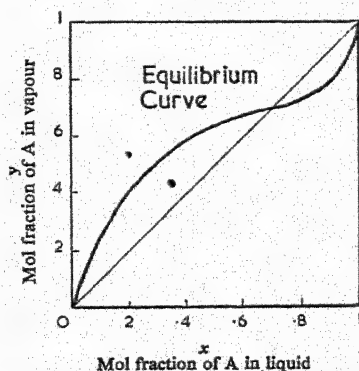
The behaviour of azeotropic mixtures may be easier to understand if we (in curve (a) Fig. 150) drop a perpendicular from M to G. We can see that the temperature composition diagram has been divided into two portions: the first is 100 per cent. B to G; the second from G to 100 per cent. A. Each section of the curve is analogous to a normal temperature composition curve (Fig. 149). We can therefore regard one section as a normal curve for a mixture of two components; one is B, the other the azeotropic mixture; the second section is a curve of the azeotropic mixture and A. So a liquid mixture falling on the first



(a) Equilibrium curve for normal type of system.



(b) Equilibrium curve for system maximum boiling-point azeotropic mixture.



(c) Equilibrium curve for system with minimum boiling-point azeotropic mixture.

section of the curve can be separated into B and the azeotropic mixture; a mixture falling into the second portion of the curve can be separated into A and the azeotropic mixture. The curve in Fig. 150 (b) can be treated in a similar fashion.

Distillation phenomena may also be studied by plotting the mol fraction (§ 268) of one component in the liquid phase (x) against the mol fraction of that component in the vapour phase (y) in equilibrium. A curve of this type may take up three general shapes as shown in Fig. 151 (a), (b), (c). Curve (a) is the normal curve; (b) the curve for the system with a high boiling azeotropic mixture and (c) a low boiling azeotropic mixture. In each graph the curve $x = y$ (which is the diagonal) is included. The point at which the equilibrium curve crosses the diagonal in curves (b) and (c) defines the composition of the azeotropic mixture. The process of distillation can be followed from the diagrams. Consider a mixture involving the normal type curve. Assume the mol fraction of one component (say A, the more volatile component) in the liquid is x_1 ; then the mol fraction of A in the vapour is y_1 . Condensing this vapour gives us a liquid in which the mol fraction of A is the same as it is in the vapour. That is it equals y_1 . Hence we get this liquid composition from the diagonal in the graph and it is x_2 . Vapourisation of this mixture gives a vapour with the mole fraction of A = y_2 . Condensation of the vapour gives a liquid with mol fraction of A = x_3 . The lines x_1 to y_1 , and x_2 to y_2 represent vapourisations: the lines y_1 to x_2 and y_2 to x_3 are condensations. The steps $x_1y_1x_2$ and $x_2y_2x_3$ are separate distillations. It can be seen that if we distil liquid of composition x_1 , take the fraction obtained from this liquid, condense it, and then repeat the process until we have carried out five distillations we will obtain a liquid of composition x_4 . We can see that the mol fraction of A in the original liquid was .1 and in the final distillate it is .95. Thus we can by successive distillations obtain a nearly pure sample of A from a mixture which originally contained a very small amount of A. Similar arguments may be applied to the curves (b) and (c) (Fig. 151).

251. Fractionating Columns. The separation of two components by collecting fractions from a simple distillation and then by redistilling these fractions is tedious. It can be simplified by the use of a fractionating column.

In industrial operations fractionation is carried out in rectifying towers or columns. Two types of column are used, packed columns and plate columns. In the former type of column intimate mixing of the vapour and liquid is achieved by packing the column with material such as coke, stone, glass, metal and many other types of substance. The packing is in a finely divided state and may have special shapes, e.g., it may be in the form of spheres, rings or helices. The working of the column depends on the fact that in the column vapour is rising up while condensed liquid is descending. The effect of the liquid and

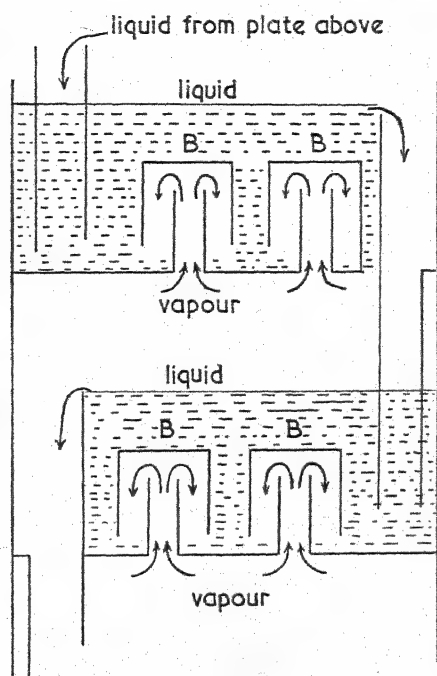


FIG. 152.

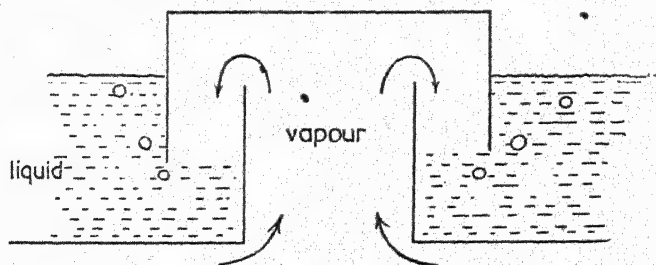


FIG. 153.

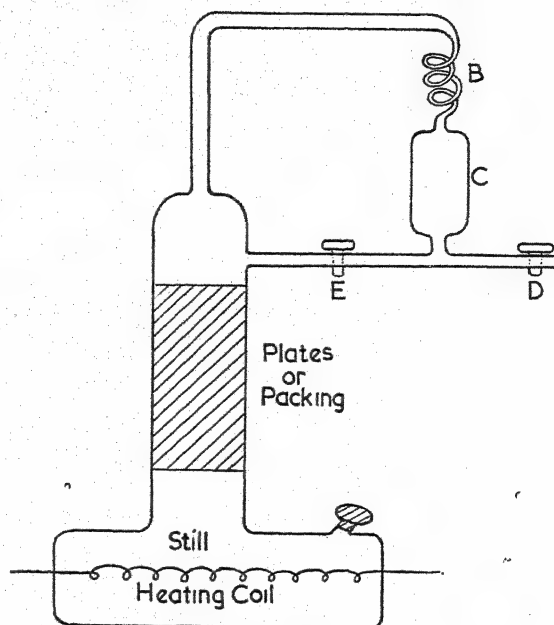


FIG. 154.

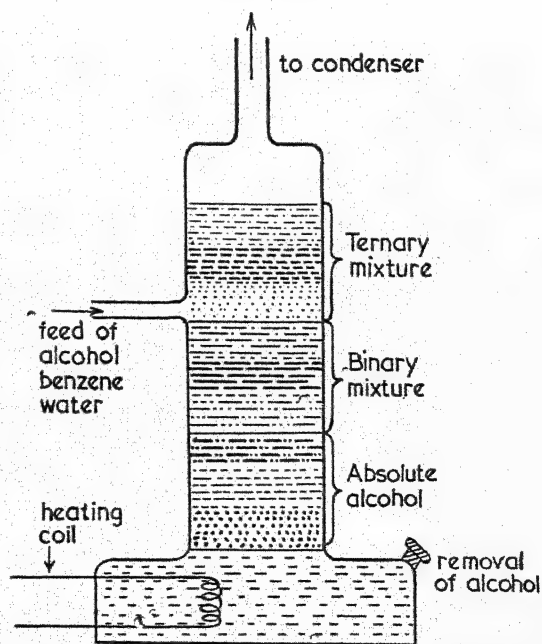


FIG. 155.

vapour intermingling is that the liquid tends to condense the less volatile constituent of the vapour; while the vapour tends to volatilise the more volatile component of the liquid. Thus, the vapour as it rises tends to contain more and more of the more volatile component: the liquid as it descends tends to contain more and more of the less volatile component. The result is that a column can separate two components very effectively.

Packed towers have the disadvantages that they are difficult to clean. Further, the packing is liable to channeling, which prevents the vapour from mixing efficiently with the liquid. The advantages of packed towers are that they are easily constructed, and for small scale work are more economical than plate columns. Packed columns are used in most laboratory work and can be constructed to give high efficiency. The columns originally used in laboratory work depended on the use of series of constrictions such as pear-shaped bulbs to impede the process of the reflux back to the still, and hence to effect a mixing of vapour and liquid. The disadvantage of such columns is that there is no control on reflux (see below).

For large scale work the plate column is generally used. The principle of this is the same as the packed column. In this type of column the mixing of liquid and vapour is carried out on metal plates. The construction of the bubble-cap plate is shown in Fig. 152. On each plate there is a layer of liquid. Liquid flows down from one plate to the next by a series of overflow pipes. The vapour rises through bubble-caps in the plates. The upward movement of the vapour through the caps prevents the liquid descending through them. The actual design of a bubble-cap is shown in Fig. 153. Plates can also be constructed with perforations in them instead of bubble-caps.

A column (see Fig. 154) is heated by a coil at the bottom. At the top of the column there is a condenser B. The liquid after condensation is collected in a collector C; it can be then withdrawn from the system through D or returned through E. The ratio of material returned to material withdrawn is called the reflux ratio. The greater the reflux ratio the greater the efficiency of fractionation by the column, but the throughput of the column is decreased. This return of material to the column permits the control of reflux in the column. Material can also be withdrawn from the bottom of the column and cuts or fractions can be collected at various heights. Modern practice is usually to collect only the top or bottom product of the column.

Columns can be designed to work on a continuous or on a batch basis. In batch distillation a definite amount of material is placed in the still portion of the column and then boiled up. No further material is supplied until the distillation of the original material is complete. In a continuous column the material is fed to the column during the actual distillation process. The feed is through a pipe into the side of the

column; the siting of the feed pipe in the column will depend on the distillation being carried out.

As an example of a distillation operation the preparation of absolute alcohol from a wash will be described. Wash contains about 7 per cent. alcohol. This can be fractionated to obtain the azeotropic mixture of alcohol and water, which contains about 96 per cent. alcohol. In order to obtain pure alcohol it is necessary to add a third substance to the mixture during the distillation. This third substance is called an entrainer. Benzene is an example of an entrainer used in alcohol production. Benzene, alcohol, and water form a ternary azeotropic mixture which boils at 65°C . Sufficient benzene is added to use all the water present in forming the ternary mixture. This is distilled off through the top of the column (see Fig. 155). Any benzene in excess of that required to form the ternary mixture with the water present will form a binary azeotropic mixture with alcohol. The binary has a higher boiling point (68.2°C .) than the ternary and hence the binary will be below the ternary in the distillation tower. Pure alcohol has a higher boiling point (78°C .) than the binary and hence will go to the bottom of the column and is drawn off there. The alcohol and benzene which distil off with the water can be recovered from the water and can then be returned to the column. The process requires in practice a complicated plant which involves four columns.

252. Vapour Pressure Curves of Partially Miscible Liquids.—A mixture of ether and water may be taken as an example. The curve is shown in Fig. 152.

When ether is added to water it first of all dissolves. If a small quantity of ether is added to water a true solution is formed, and the

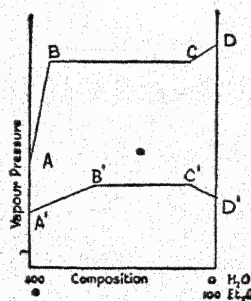


FIG. 156. — Vapour Pressure - Composition Curve for a Mixture of Partially Miscible Components.

total vapour pressure of the mixture increases as shown by the line AB. But, as more ether is added, the water becomes saturated, and a layer of ether is formed, i.e., a new phase is produced. Now, according to the Phase Rule, the system must become univariant, for we have three phases (ether in water, water in ether, vapour) and two components (ether and water). This means that the vapour pressure will remain constant whilst the composition varies. This is the line BC in the curve. At a point C, sufficient ether will have been added to dissolve all the water, and there is now a saturated solution of water in ether. From this point the vapour pressure will rise to that

of pure ether at D. In other systems the curve may fall as in the lower curve A'B'C'D'.

253. Vapour Pressure of a Mixture of Immiscible Liquids.—It is

obvious that here we have three phases throughout the whole range of compositions, and two components. Hence, according to the Phase Rule, the system is univariant, and vapour pressure is constant for all compositions. The vapour pressure curve is therefore a straight line parallel to the composition axis. The curve is really the same as that just considered (Fig. 157), except that the sloping portions have become very short.

The vapour pressure AB will be the sum of the partial pressures of the two components. Thus, at a temperature of 80° C., the vapour pressure of water is 356 mm., whilst that of bromobenzene is 66 mm. The vapour pressure of a mixture of these two would therefore be 422 mm. at 80° C.

254. Steam Distillation.—This property of a mixture of immiscible liquids is made use of in the process of steam distillation, the object of which is to separate organic substances from undesirable impurities which would be difficult to remove in other ways, or to distil an organic body without submitting it to too great a temperature or resorting to vacuum distillation.

The apparatus is illustrated in Fig. 158. It consists of a boiler A, the steam generated therein being passed into the large flask B containing the mixture to be separated. This is connected by an outlet tube to a Liebig's condenser in the usual way. Finally, to obtain the pure product it must be separated in a separating funnel from the water which also comes over, and then dried and redistilled.

The amounts of water and substance which distil over can readily be calculated. Suppose that, at the boiling point of the liquid, the vapour pressures of the two components are p_1 and p_2 . The volumes of vapour produced will be proportional to these pressures. The densities of the vapours are proportional to their molecular weights, so the ratio of

weights of the substances distilling is $\frac{M_1 p_1}{M_2 p_2}$, M_1 and M_2 being the

molecular weights of the liquids.

This is best illustrated by a numerical example. A mixture of nitrobenzene and water boils at 99° C. The molecular weight of nitrobenzene is 123, and the vapour pressure of water at 99° C. is 733 mm. Hence, assuming that the pressure of the atmosphere is normal, *viz.*, 760 mm., the vapour pressure of the nitrobenzene must be 27 mm. The ratio by weight in which the two liquids distil is

$$\frac{\text{Nitrobenzene}}{\text{Water}} = \frac{123 \times 27}{18 \times 733} = \frac{1}{3.97}$$

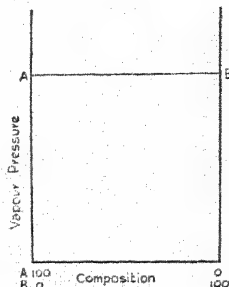


FIG. 157. — Vapour Pressure - Composition Curve for a System of two Immiscible Liquids.

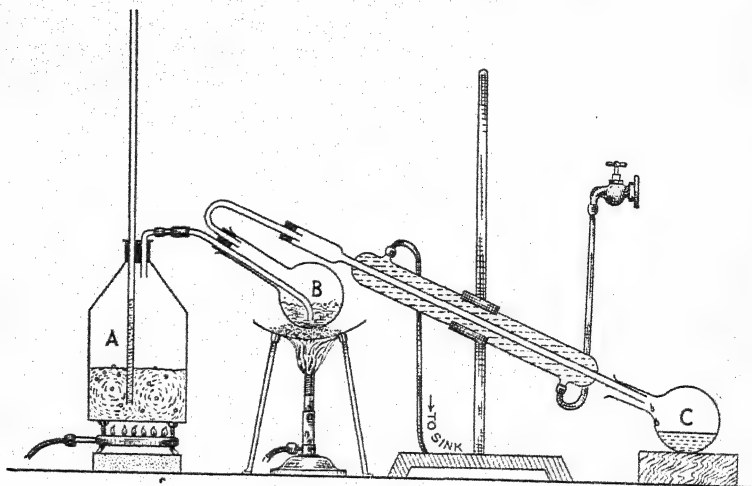


FIG. 158.—Apparatus for Steam Distillation.

It is obvious that water is a good liquid to use in this connection, because it has a low molecular weight.

The reverse calculation is sometimes used for finding the molecular weight of a liquid which is not miscible with water. Thus, a mixture of bromobenzene and water distils at 95.2°C. , at which the respective vapour pressures are 119 and 641 mm. The ratio by weight in which the liquids distil is bromobenzene: water = 1.62 : 1. If M is the molecular weight of the bromobenzene,

$$\frac{\text{Bromobenzene}}{\text{Water}} = \frac{1.62}{1} = \frac{M \times 119}{18 \times 641}$$

Hence, $M = 157.1$.

E. SOLUTIONS OF SOLIDS IN LIQUIDS

255. General.—It is not possible to say with any certainty why a solid dissolves in a liquid. It is clear that the solubility or insolubility is not directly connected with the solute only, but that it is determined by both solute and solvent; for many substances which are insoluble in water will dissolve in other solvents, and *vice versa*. The regular decrease in solubility with increase in atomic weight or atomic number in a family of elements, *e.g.*, calcium, strontium, barium and radium sulphates in water, indicates that solubility is connected with atomic number, and therefore with the number of extra-nuclear electrons in the metal atom, and the resultant electric field of the atom and molecule. There can be no doubt that solution depends upon the weakening

of the electrical forces which ordinarily preserve the shape of the crystal lattice. As mentioned in § 131, Tammann has shown that a crystal does not immediately break down on dissolution into molecules, but remains in "lattice blocks" of ultramicroscopic dimensions. These ultimately break up into molecules. The electrical properties of the solvent, then, must be such as to weaken these electrical crystal forces which are due to the electrical fields of the molecules themselves. The solution to the problem of why some substances dissolve in a certain solvent and others do not is to be found in a study of the electrical properties of both solute and solvent, but our present knowledge is insufficient to enable us to give any definite answer.

The simplest external electrical property which can be measured, and can give any indication of the internal electrical field of a molecule, is the dielectric constant, and as far back as 1906 Walden suggested that the molecular solubility of a solute was related to the dielectric constant (ϵ) by the expression

$$\frac{\epsilon}{\sqrt[3]{S}} = K,$$

where K is a constant and S is the molecular solubility of the solute expressed as a percentage, and given by the equation

$$S = \frac{100n}{n + N},$$

n and N being the numbers of gram-molecules of solute and solvent respectively in the solution.

According to this equation, liquids which have the higher dielectric constants should be the better solvents, and this is borne out in practice, as shown by the following data.

TABLE LXX.—SOLUBILITY OF POTASSIUM IODIDE IN VARIOUS SOLVENTS (Walden)

Solvent.	Formula.	ϵ .	Solubility, gms./100 gms. solvent. 25° C.
Water	H ₂ O	81	59.54
Methyl alcohol	CH ₃ OH	35.4	14.97
Acetonitrile	CH ₃ CN	36.4	2.00
Ethyl alcohol	C ₂ H ₅ OH	26.8	1.92

However, numerous exceptions have since been discovered, and the Walden expression is no longer considered correct, but there is no

doubt that dielectric constant, though not the only factor deciding solubility, must rank among the most important of these.

In dealing with organic bodies, it is frequently found that the substitution of one group or atom by another converts the substance from a soluble into an insoluble compound, and *vice versa*. Thus, benzene is insoluble in water, but when one hydrogen atom is replaced by hydroxyl, the phenol produced is fairly soluble. The increased solubility is no doubt due to the affinity of the phenolic — OH group for water.

It is interesting to note that whilst organic substances containing hydroxyl are nearly all soluble in water, inorganic hydroxides are nearly all insoluble.

256. Determination of Solubility.—The solubility of a substance is the maximum weight of it which will dissolve in 100 gms. of the solvent at a given temperature.

To determine this it is necessary to prepare a saturated solution of the solute and then analyse it.

It is easy to devise a suitable method where accuracy is not important. A saturated solution is prepared by shaking an excess of the solute with the solvent in a flask placed in a thermostat regulated to the required temperature. When the solution is saturated, some of it is removed by means of a pipette, provided with a plug of cotton wool or glass wool, to prevent any solid from being withdrawn. The solution withdrawn is placed in a dish of known weight and then weighed again. The solution is then evaporated to dryness and re-weighed. The difference between the weight of the dish alone and that of the dish and solid gives the weight of solute in the solution. The difference between the weight of the dish alone and that of the dish and solution gives the weight of the solution. The weight of solvent is the difference between the weight of solution and that of the solute. From these figures the solubility can be calculated.

It is clear that a number of errors are possible with this simple method. In the first place, the withdrawal involves a cooling, and some solid will be deposited in the pipette and may not be transferred to the dish. To overcome this, the pipette may be warmed in the thermostat before use. Also, the evaporation of a liquid to dryness is a highly undesirable operation to introduce

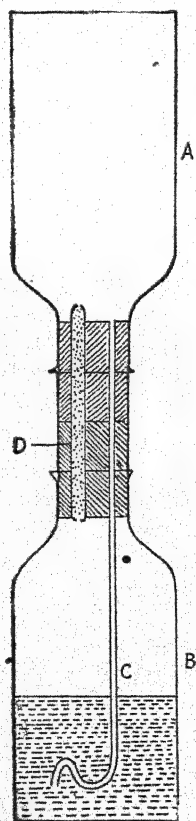


FIG. 159.—Apparatus for determining solubility.

into quantitative work, as it is so easy to lose liquid by spirting. This can be obviated by making use of some chemical method of analysis, where available.

An apparatus which has been used to determine the solubility of solids to a high degree of accuracy is shown in Fig. 159.

The apparatus is due to A. N. Campbell (*J. C. S.*, 1930, 179), and consists of two 1-oz. wide-mouth reagent bottles, A and B, provided with corks and arranged as shown. The mouth of A is ground. Glass tubes pass through the corks, D being a tube of about 3 mm. diameter, constricted at the upper end, and packed with glass wool, and C is a piece of quill tubing drawn out to a capillary and bent to an S shape, not, however, sealed off.

The bottle B is charged with solid and solvent, and fixed in the position shown in the diagram on the horizontal paddle of a thermostat stirrer. When dissolution is complete, the apparatus is inverted in the thermostat, and the solution filters through the plug, air coming into the top vessel, then B, through the capillary C. The liquid entering C at first is pure solvent, which will dilute the saturated solution when expelled by the air pressure from below, so it is advisable to have the tube as fine as possible. The very small amount of solvent contained by it will then be negligible, but in any case it will have a chance of becoming saturated before passing into the lower bottle, then A. The S bend in the tube prevents the admission of solid into A. When the solution has passed through, the apparatus is removed from the thermostat, and the weighed bottle A closed with a ground glass plate. The solution can then be analysed.

Where high temperatures are to be used, it is advisable to wire down the corks, as they may be forced out by the pressure.

For the determination of the solubility of sparingly soluble salts several methods are available. Most of these are fully dealt with in other sections. They can be summarised as:—

I. Electrical methods. (a) Determination of the solubility product by the E.M.F. method (see § 340). (b) Determination of conductivity of the solution (see § 298).

II. Colorimetric method. This depends on comparing the depth of colour of a solution with that of some standard solution. For example to determine the solubility of lead sulphate, a quantity of it is shaken up with water, the solution filtered, and then hydrogen sulphide is passed through it to form lead sulphide. This is brown in colour; it will not be formed in sufficient quantity to give a definite precipitate, but the solution will be coloured brown through the presence of colloidal lead sulphide. The colour of this solution is compared with that obtained by passing hydrogen sulphide through a solution of lead acetate containing a very small, but known, lead ion concentration. The standard solution is progressively diluted, until the correct colour is reached, when the lead ion concentration in the unknown solution is obtained.

III, Radioactive method. The method of radioactive indicators devised by Hevesy and Paneth finds some application in the determination of the solubility of sparingly soluble salts. A solution of a soluble salt of the metal of which the sparingly soluble substance is a salt is prepared, and a small known quantity of a radioactive substance is added. The sparingly soluble salt is then precipitated by the addition of the proper reagent, and it brings down with it the radioactive substance. It is filtered off, dried and weighed. A portion is then mixed with water in an ordinary solubility apparatus, such as that described above, and a saturated solution is prepared. A known volume of the solution is removed and evaporated to dryness, and the activity of the residue is determined by means of an electroscope or Geiger counter. The activity is proportional to the amount of salt present, and, since a known amount of indicator was added to start with, the activity

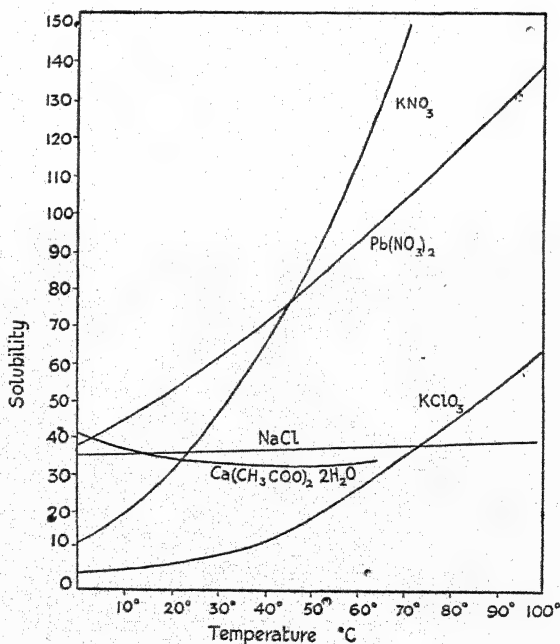


FIG. 160.—Solubility Curves.

associated with a given weight of the salt is known, and the amount of substance present can be calculated. The method is very sensitive, and has afforded good results, particularly in the determination of the solubility of lead and barium salts (see also § 54).

A satisfactory method for the rough determination of the solubility

of a sparingly soluble salt in the laboratory is to take a known weight of the salt and agitate it with one litre of water for some time at the temperature required. Filter off through a quantitative paper, and weigh the residue after drying. The difference in weight gives the amount dissolved by one litre of water.

257. The Solubility Curve and its Characteristics.—The solubility curve is the curve drawn between solubility and temperature. It may take a number of different forms. They may be considered in two sections: first, those which are continuous and, secondly, those which are discontinuous.

I. Continuous Solubility Curves.—A number of these are shown in Fig. 160.

As a rule, solubility increases considerably with the temperature. This is shown in the curves for lead nitrate and potassium chlorate. Common salt is an exceptional case, the solubility increasing very little with temperature. A few substances are known, chiefly the calcium salts of organic acids, of which the solubility decreases with increase in temperature. Examples are calcium acetate and calcium butyrate. Calcium sulphate has a peculiar solubility curve. Whilst continuous it shows a maximum, so that up to a certain temperature the solubility increases with temperature, and above that it decreases again.

The effect of temperature on the solubility of a substance which undergoes no chemical change with temperature can be predicted from a knowledge of its heat of solution. The heat of solution of most salts is positive, *i.e.*, heat is absorbed when the substance goes into solution. According to Le Chatelier's principle (§ 149), if the temperature of a saturated solution containing some of the solid salt is increased, a change will take place in the equilibrium to annul the effect of the increase in temperature, *i.e.*, that change will take place which absorbs heat. Now the process that absorbs heat is the dissolution of the solid salt, and so more dissolves. If the heat of solution is negative, as it is in the case of many calcium salts of the fatty acids, then the reverse process will take place, for the dissolution of salt now involves absorption of heat.

On the basis of thermodynamics, it has been shown that the heat of solution and the solubilities of a substance at two given temperatures are connected by the equation

$$\log_e \frac{s_1}{s_0} = -\frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_0} \right)$$

where T_0 and T_1 are the temperatures, on the absolute scale, s_0 and s_1 are the solubilities at these temperatures, R is the gas constant, and ΔH the heat of solution. This equation, it will be noted, is exactly similar to that given by Arrhenius for the effect of temperature on the rate of a reaction (§ 201).

This equation can readily be tested if the necessary data are given. Thus, at 0°C ., the solubility of succinic acid in water is 2.88, whilst at 8.5°C . it is 4.22. Taking R as 2 gm.-cals. per degree, we have, substituting in the above equation,

$$2 \log \frac{4.22}{2.88} = \Delta H \left(\frac{1}{273} - \frac{1}{281.5} \right),$$

$$\Delta H = 6,863 \text{ gm.-cals.}$$

The observed value for the heat of solution of succinic acid is 6,700 gm.-cals., agreeing very well with that calculated.

II. Solubility Curve Discontinuous.—The solubility curve may, however, not be continuous, but may show sudden changes of direction. Whenever this occurs, it indicates that the solid phase in contact with the saturated solution has altered its character in some way, and that we really have to deal with two distinct solubility curves, which meet at a point. The temperature indicated by this point is that at which the transition from the one state to the other takes place. This alteration may be a polymorphic change or a change in hydration of the *solid* substance.

As an example of the effect of a polymorphic change on the solubility curve we may take ammonium nitrate. Within the range 10° to 50°C ., this substance changes its crystalline form. Actually this is only one of

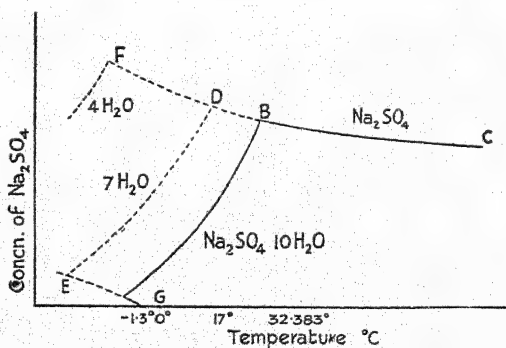


FIG. 161.—Solubility of Sodium Sulphate.

five such changes. When the solubility curve of this substance is plotted it is found to exhibit a distinct break at 32°C ., the transition temperature of the β -rhombic into the γ -rhombic form (Fig. 98). Another substance with a very similar solubility curve, showing a break due to polymorphic changes, is thallium picrate.

The other cause of breaks in the solubility curve, *viz.*, change in the degree of hydration of the solid in contact with the saturated solution,

is considerably more common. One of the best examples is sodium sulphate (Fig. 161). If the solubility curve of sodium sulphate is plotted, it is found to have a very sharp break at 32.383°C ., at atmospheric pressure. At this point there is an equilibrium in the solid state between the decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and the anhydrous salt, so that below this temperature the solubility curve is that of sodium sulphate decahydrate, and above it it is that of anhydrous sodium sulphate. The curve CB can be followed backwards a short distance by seeding the saturated solution with the heptahydrate, so that the metastable portion BD is realised, and it is then possible to follow the solubility curve of the metastable heptahydrate DE.

Consider the complete solubility curve of a substance like silver nitrate (Fig. 162). The solubility of this salt above 100°C . has been studied by Etard and by Tilden and Shenstone. The solubility increases with temperature, and there is a break in the solubility curve at 160°C ., due to the formation of a new crystalline form. The curve continues until, for 100 per cent. silver nitrate, the temperature is the melting point of the salt, *viz.*, 208°C . This part of the curve, BCD, represents the equilibrium between salt, solution, and vapour. Now consider the other branch of the curve. Water freezes under atmospheric pressure at 0°C ., but, if a small quantity of silver nitrate is added to the water, its freezing point is lowered, and the more salt added the lower is the freezing point. At last, however, a point is reached when the silver nitrate no longer dissolves, and is deposited along with the ice. At this temperature we have four phases, vapour, solution, salt, and ice, all in equilibrium, and the system is therefore non-variant, as there are two components. The point B is thus a quadruple point. It may be regarded as the point of intersection of the solubility curve and the freezing-point curve. It is clear that this point B is the lowest temperature that can possibly figure on the solubility curve; it is the lowest temperature that can be attained with mixtures of two components in the presence of vapour. It is usually called the *cryohydric point*, or the eutectic point (§ 220). There is clearly no distinction between solutions of water in liquid silver nitrate and of silver nitrate in water, in the right-hand limb of the curve.

For some time it was thought that the substance which was deposited at the cryohydric point was a definite chemical compound of the salt and water, and it was called a *cryohydrate*. Offer, however, showed that

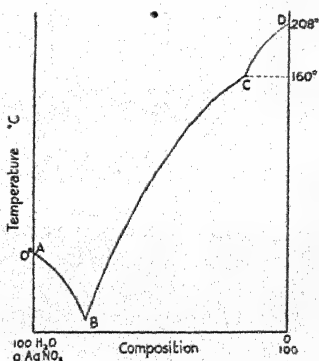


FIG. 162.—Solubility of Silver Nitrate.

although these substances appeared to be compounds, because they possessed a constant melting point, they were actually mixtures. This was indicated by the fact that the heat of solution of the cryohydrate was the sum of the heats of solution of the ice and salt, in the proportion in which they are contained in the so-called "compound", and that similarly the specific volume of the cryohydrate was that calculated for a mixture. Also, the separate crystals of ice and salt can be distinctly seen, when the cryohydrate is examined under the microscope, particularly when the salt is coloured, *e.g.*, potassium permanganate.

This has an important bearing on the preparation of freezing mixtures. Until the "cryohydrate" separates we are dealing with a univariant system, and hence, if the temperature is altered, the composition of the phase in equilibrium will vary. Similarly, if the composition is varied, the temperature must alter. If ice is added to the univariant system salt—solution—vapour, the temperature must fall and the ice melt, and if enough ice is added the cryohydric temperature will ultimately be reached, provided that solid salt is added as fast as it dissolves. Similarly, if salt is added to the system ice—solution—vapour, the concentration of the salt will increase, ice will melt, and the temperature will fall, and again this will take place until the cryohydric temperature is reached, when the four phases can be in equilibrium.

In the preparation of freezing mixtures, both these methods can be used. In either case, there is an absorption of heat, and the temperature falls to the cryohydric point, which is the lowest temperature that can be attained. In practice, this temperature is very rarely reached owing to radiation, and absorption of heat by the solution formed. The latter can be counteracted by allowing the solution to drain off as soon as it is formed, and the former by increasing the rate of cooling, which can be brought about to a certain extent by rapid and intimate mixing of the components. Hence, it is better to use snow than ice in preparing a freezing mixture.

It is possible to have four phases present in a system of the type now under consideration, without ice being one of them. This is so where there is a change in the solid phase, as with sodium sulphate. Thus, at the point B in the solubility curve of sodium sulphate (Fig. 161), there are the phases anhydrous salt—hydrated salt—solution—vapour, and it is in fact a eutectic point, just as when one of the phases is ice. Where there is a possibility of the formation of a large number of hydrates before the salt melts, there are a number of these eutectic points in the solubility curve. This is well shown in the case of ferric chloride, the solubility curve of which is given in Fig. 163.

The curve AB shows the effect of adding ferric chloride to ice. It is, in fact, the freezing point curve of ferric chloride solutions, and B is the cryohydric point, -52°C . If the solution is allowed to warm, and ferric chloride is added to keep the solution saturated, the curve BC is

followed. This is the solubility curve of the dodecahydrate. At C this compound melts completely, and addition of anhydrous ferric chloride results in the formation of the compound $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$. The solubility curve falls until the point D is reached where, there are again four phases, the dodecahydrate, $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$, existing in equilibrium with the heptahydrate, $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$. This is in reality, then, another eutectic point. If the solution is warmed, more ferric chloride will dissolve, and a similar curve is followed through E to F, the eutectic point for the hydrates $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$. This goes on until finally the curve is the solubility curve of anhydrous ferric chloride, ending at the melting point of the pure salt. Points such as C, G, E and I are called congruent melting points.

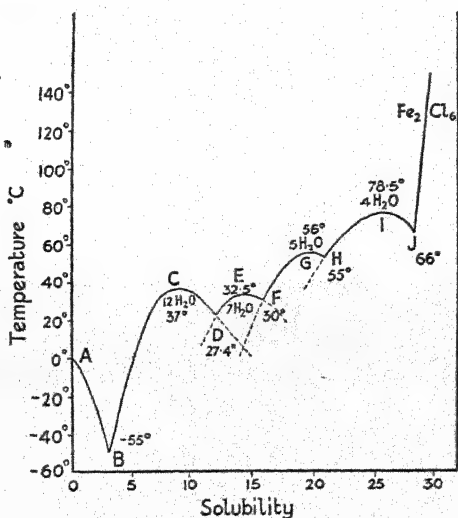


FIG. 163.—Solubility of Ferric Chloride Hydrates.

The various parts of this curve can be looked upon in a slightly different way. Starting from the point C, the curve CB represents the effect of adding water to $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$, and therefore involves a lowering of the freezing point, whilst the curve CD represents the addition of ferric chloride to it, which again must lower the freezing point, so the curve drops away on both sides of the point C. Similar explanations can be given for the other humps.

It is clear that the number of these humps that can be detected on the solubility curve indicates the number of hydrates which are capable of existing in the solid state, and this therefore provides a valuable method of investigating hydrates. It must be clearly understood,

however, that the solubility curve gives no evidence whatever as to the existence of hydrates in solution.

The dotted lines in the curve of solubility of ferric chloride represent metastable states that have been realised experimentally by taking the necessary precautions.

258. Supersaturation and Suspended Transformation.—The occurrence of a point such as B in the solubility curve of sodium sulphate (Fig. 161), or D, F, H, or J in the solubility curve of ferric chloride (Fig. 163), depends upon the co-existence of four phases. Sometimes the fourth phase does not appear, and consequently the point is not obtained. Thus, it is possible to follow the dotted lines in the two solubility curves just mentioned, since the fourth phase is not always formed. On cooling a solution of sodium sulphate from above the transition temperature, say 32.6°C ., to room temperature, the hydrated form, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, may not be produced at this temperature, so the solubility curve may be continued along the dotted line to D, and with great care even to F. It is thus possible to follow the solubility curve of a substance past the point at which it ceases to be the stable form. It is seen from the curves drawn that the solubility of the metastable form is greater than that of the stable form. This is analogous to the vapour pressures of stable and metastable states (§ 144). It is clear then that a solution of a metastable form must be more than saturated (supersaturated) with respect to the stable form. If the fourth phase is added to the solution in the form of a small crystal of the stable form, it follows that deposition of the stable form must take place until the concentration of the solution corresponds to the solubility of the stable form. It is therefore easy to bring about the deposition of the stable form from a solution containing the metastable form merely by adding a crystal of the phase required.

A similar case to this is the failure of some saturated solutions to deposit crystals when they are cooled beyond the point at which crystals would normally appear. This gives rise to supersaturated solutions. This behaviour is usually found with salts which crystallise with water of crystallisation. It is rarely found with anhydrous salts, though a good example of an anhydrous salt which easily forms a supersaturated solution is sodium chlorate.

The crystallisation of a solution which is supersaturated is readily brought about by the addition of a small crystal of the solute, or by the addition of dust particles or other nuclei about which crystallisation can take place. It is therefore a difficult matter to preserve a supersaturated solution in air, unless only air which has been filtered from dust particles is allowed to come into contact with the solution. Deposition of crystals from a supersaturated solution can also be brought about by mechanical disturbance, such as shaking, or rubbing the walls of the vessel with a glass rod (see also § 151).

259. Effect of Pressure on Solubility.—It is to be expected that solids which dissolve in a solvent with contraction of volume will show an increase in solubility when pressure is applied, and that, conversely, substances which dissolve with increase in volume will suffer a decrease of solubility if pressure is increased. This is a direct consequence of the principle of Le Chatelier (§ 149), and has been verified experimentally. Thus, when sodium chloride dissolves in water there is a contraction. At a pressure of 1 atmosphere the solubility at 18°C. , expressed as the number of grams of salt in 100 gms. of solution, is 26.4. At a pressure of 500 atmospheres the solubility increases to 27.0.

260. Effect of Particle Size on Solubility.—When preparing a solution, the solute is usually powdered in order to increase the rate of solution. It is obvious that if the solvent can be in contact with a greater surface it will be able to dissolve the solid more quickly. In addition to assisting the rate of solubility, the particle size also makes a difference to the actual solubility. A saturated solution of calcium sulphate at 18°C. contains 2.085 gms. of the salt per litre when the particles are of ordinary size, but this increases to 2.476 gms. when the particles are reduced to a diameter of $0.3\ \mu$ ($1\ \mu = 1\text{ micron} = 0.0001\text{ cm.}$), about one-seventh of the ordinary size. The solubility of barium sulphate is almost doubled when the particle size is reduced from a diameter of $1.8\ \mu$ to $0.1\ \mu$. This is clearly of importance in quantitative analysis. The more granular the precipitate the less will be lost in the washing processes.

The reason for this change in solubility lies in the increase in surface forces when the particles are smaller. It is well known that the pressure inside a bubble is greater the smaller is the bubble. In fact, the pressure is given by $2T/r$, where T is the surface tension and r the radius of the bubble, supposed formed inside a liquid. Now it must be supposed that similar forces to surface tension act at the surface of a solid. There is a great deal of evidence for this view based on adsorption, catalysis and other phenomena. If this is so, there must be a greater tendency for the smaller particle to expand, or to dissolve, since by that means it can reduce this internal pressure. Hence, it will be more soluble than the larger particles.

In the measurement of the E.M.F. of cells in which the electrodes are covered with a fine powder, the increased solubility of finely powdered substances has frequently been noted. If a cell is made up of two calomel electrodes, the electrode covered with the more finely powdered salt becomes positive with respect to that covered with the coarse salt, owing to the difference in solubility (§ 338).

Reactions also proceed more rapidly when the reactants are finely powdered. This is probably due to increased surface forces.

261. Distribution of a Solid between two Non-miscible Solvents.—It has already been shown that in a system gas—liquid, the gas distributes

itself in a definite ratio between the liquid itself and the space above the liquid, the concentration of the gas in the space above the liquid, divided by that of the gas in the liquid, being a constant. This is Henry's Law (§ 233). An identical law holds for the distribution of a solid or liquid between two liquids. When a liquid or solid distributes itself between two liquids, the ratio of the concentrations in the two liquid phases is constant, provided the substance dissolves in both solvents in the same form, *i.e.*, provided that no chemical combination takes place between the solute and either of the solvents, and that no association or dissociation takes place. Stated mathematically,

$$c/C = K,$$

where c is the concentration in one solvent and C that in the other. K is called the distribution coefficient, or partition coefficient. This is known as the *Distribution Law* (or sometimes the Partition Law) and is simply Henry's Law applied to solid or liquid instead of gas.

It is seldom found that the values of c/C are strictly constant through a series of determinations with different concentrations. The instances in which the ratio is reasonably constant over a considerable range which have been investigated include the distribution of hydrogen peroxide between water and some organic liquids, boric acid between amyl alcohol and water, iodine between water and chloroform, bromine between water and bromoform, iodine between water and carbon disulphide, and phenol between water and amyl alcohol. It is not difficult to devise methods for analysing the phases in all these instances.

As with Henry's Law for gases, the Distribution Law does not hold where any change in the molecular condition of the distributed substance occurs when it dissolves in either solvent. The difficulty with liquid systems is that the corrections frequently have to be made in both liquids. The principle to be used is that the Distribution Law holds for those molecular species which are identical in the two solvents.

Consider first the instance where the substance *dissolves without dissociation in liquid A, but dissociates in liquid B.*

Let C_1 be the concentration of undissociated molecules in A , C_2 the total concentration in B , determined by analysis, and α the degree of dissociation. Then, by the ordinary law, the concentration of undissociated molecules in B must be $C_2(1 - \alpha)$. Only the undissociated molecules can be in equilibrium, as there are no dissociation products in A to be in equilibrium with those in B .

Hence,

$$\frac{C_1}{C_2(1 - \alpha)} = K.$$

If there is *dissociation in both liquids to different extents*, the problem

becomes more complicated. Thus, let α_A be the degree of dissociation in liquid A, and α_B the degree of dissociation in liquid B. Let the concentration of the substance as determined by analysis (*i.e.*, total of undissociated and dissociated molecules) in liquid A be C_A , and in liquid B, C_B . Then, by the Law of Mass Action (§ 196), assuming the dissociation to take place into two components, we have

$$\frac{[\alpha_A C_A]^2}{(1 - \alpha_A) C_A} = K_1 = \frac{C_A \alpha_A^2}{1 - \alpha_A},$$

Hence,
$$\alpha_A = \frac{-K_1 + \sqrt{K_1^2 + 4K_1 C_A}}{2C_A} \quad (1)$$

Similarly, for liquid B

$$\frac{[\alpha_B C_B]^2}{(1 - \alpha_B) C_B} = K_2 = \frac{C_B \alpha_B^2}{1 - \alpha_B}$$

and
$$\alpha_B = \frac{-K_2 + \sqrt{K_2^2 + 4K_2 C_B}}{2C_B} \quad (2)$$

Now, by Nernst's statement, the undissociated molecules in A will be in equilibrium with those in B. Hence,

$$\frac{C_A (1 - \alpha_A)}{C_B (1 - \alpha_B)} = K \quad (3)$$

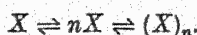
Substituting for α_A and α_B from (1) and (2), we have

$$\frac{C_A - \frac{\sqrt{K_1^2 + 4K_1 C_A}}{2} + \frac{K_1}{2}}{C_B - \frac{\sqrt{K_2^2 + 4K_2 C_B}}{2} + \frac{K_2}{2}} = K \quad (4)$$

or
$$\frac{2C_A + K_1 - \sqrt{K_1^2 + 4K_1 C_A}}{2C_B + K_2 - \sqrt{K_2^2 + 4K_2 C_B}} = K \quad (5)$$

We have two methods of testing this expression. Either we can work from equation (3) or from (5), according to the data at our disposal. If we know the degrees of dissociation we shall use equation (3). If we know the equilibrium constants we shall use (5).

Let us consider now the case of *association in one phase* and normal solution in the other. The reaction occurring may be represented as



If we analyse the phase in which normal solution has occurred, we shall obtain the concentration of the simple molecules in that phase (C_1), but if we analyse the other phase we find not only the concentra-

tion of single molecules, but also that of associated molecules. We have to find from this the concentration of single molecules only. Let the total concentration in this phase be C_2 . By applying the Law of Mass Action to the equilibrium in this phase, we find, if α is the degree of dissociation of associated into simple molecules,

$$\frac{(C_2\alpha)^n}{C_2(1-\alpha)} = K_1; \quad C_2\alpha = \sqrt[n]{K_1 C_2(1-\alpha)}.$$

But $C_2\alpha$ is the concentration of simple molecules in the second phase, and hence the Distribution Law states

$$\frac{C_1}{C_2\alpha} = K = \frac{C_1}{\sqrt[n]{K_1 C_2(1-\alpha)}}$$

whence we have the relationship

$$\frac{C_1}{\sqrt[n]{C_2(1-\alpha)}} = K'.$$

We can thus determine the degree of association in a solution. The above calculations apply whether the dissociation is of complex molecules into simpler ones (as supposed in the calculation), or if it is electrolytic.

It is easy to work out the other cases where we have combinations of these already given. The results are given in tabular form below:—

Phase I C_1	Phase II C_2	Relationship
Normal . . .	Normal . . .	$K = \frac{C_1}{C_2}$
Normal . . .	Association	$K = \frac{C_1}{\sqrt[n]{C_2(1-\alpha)}}$
Dissociation . . .	Association	$K = \frac{C_1(1-\alpha)}{\sqrt[n]{C_2(1-\alpha)'}}$
Normal . . .	Dissociation	$K = \frac{C_1}{C_2(1-\alpha)}$

It must be remembered that in all these cases we have assumed that the Law of Mass Action (§ 196) holds, and that the species distributed is the simple molecule.

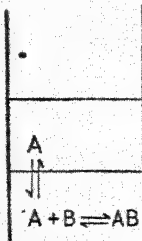


FIG. 164.

It is clear that the experimental study of the distribution of a substance between two liquids may prove instrumental in deciding whether it is associated or dissociated in any particular solvent and to what extent this change has taken place. In the case of electrolytic dissociation it is not so easy to use the method, since it is unusual to find a strong electrolyte which will also dissolve in a liquid which is not miscible with water.

Distribution may also be used in the study of other

equilibria. Thus, the equilibrium constants of some reactions can be determined. Suppose we have a substance A, which will distribute itself between two solvents, and suppose that in the second solvent there is another substance, say B, with which A can form a compound AB. Suppose the upper layer contains z gms. of A. This is known by analysis. Let the bottom layer contain initially x gms. of A and y gms. of B. If the distribution coefficient is C , the bottom layer must contain Cz gms. of A, assuming the volume of both layers to be the same. Hence $x - z - Cz$ gms. of A must have combined to form AB. The weight of AB can thus be calculated, and the weight of free B deduced. This gives all the data required for calculating the equilibrium constant.

The use of the method in the determination of the degree of hydrolysis of salts is described in § 328, in connection with the degree of hydrolysis of aniline hydrochloride.

The reaction between iodine and potassium iodide in the formation of I_3^- ions has been studied by investigating the distribution of iodine between an organic solvent, such as chloroform, and an aqueous solution of potassium iodide. In a similar way, the existence of the Br_3^- ion in aqueous solution has been shown, and the hydrolysis of chlorine ($H_2O + Cl_2 \rightleftharpoons HCl + HOCl$) has also been studied. Dawson showed the existence of the compound $CuSO_4 \cdot 4NH_3$ by investigating the distribution of ammonia between chloroform and aqueous solutions of copper sulphate.

Although this method can be widely used, it must be borne in mind that a knowledge of the equilibria occurring in each phase is necessary if trustworthy results are to be gained.

262. The Process of Extraction.—In organic chemistry, when it is necessary to separate a substance from a solution, recourse is frequently had to the process of extraction, in which the solution containing the substance required is shaken up with some solvent in which the required substance is more soluble, and the solutions separated. This is an example of the application of distribution.

It is frequently asked whether it is more economical to extract with all the solvent available in one operation, or to use it in several portions, separating each time. Thus, suppose we require to extract some succinic acid from aqueous solution with ether, and there is a given volume of ether at our disposal. Will it be more economical to use all the ether at once, or to use it in a number of portions?

This question can be answered by a simple calculation. Let W c.c. of a solution, containing x_0 gms. of substance, be extracted with A c.c. of a solvent. Let x_1 be the number of grams of unextracted substance. Then, the concentration of the substance in the extracting liquid will be

$$\frac{x_0 - x_1}{A},$$

and in the original solution

$$\frac{x_1}{W}$$

Hence, by the Distribution Law,

$$K = \frac{\frac{x_1}{W}}{\frac{x_0 - x_1}{A}}$$

$$\therefore x_1 = \frac{KW(x_0 - x_1)}{A} = x_0 \frac{KW}{KW + A}$$

After a further extraction, with A c.c. of solvent, suppose that x_2 gms. remain in the original solution. Then,

$$x_2 = x_1 \frac{KW}{KW + A} = x_0 \left(\frac{KW}{KW + A} \right)^2$$

After the n th extraction, the quantity unextracted will be

$$x_n = x_0 \left[\frac{KW}{KW + A} \right]^n$$

If all the extracting liquid had been used at once,

$$\frac{\frac{x_n}{W}}{\frac{x_0 - x_n}{nA}} = K; \quad x_n = x_0 \frac{KW}{nA + KW}$$

and thus it is more economical to use it in portions. A numerical example will make this quite clear. An acid A is to be extracted from aqueous solution, in which it dissolves without dissociation, by means of ether. Fifty grams of the acid are dissolved in 1 litre of water. The distribution coefficient of the acid between ether and water is 3. One litre of ether is to be used in the extraction. Compare the amounts of acid left in the aqueous solution, (a) after extraction with the whole of the ether at once, and (b) after extraction with five portions of 200 c.c.

Case (a). Extraction with all the ether at once. Let x be the concentration in grams per litre in the ether layer. Then, by the Distribution Law,

$$\frac{x}{50 - x} = \frac{3}{1}$$

$$x = 37.5.$$

Hence, the amount left will be 12.5 gms.

Case (b). Extraction in five portions of 200 c.c. Let x be the concen-

tration in grams per litre in the ether layer in the first extraction. This time there are only 200 c.c. of ether, and so the actual weight extracted will be $x/5$ gms., leaving the concentration in the aqueous layer $(50 - x/5)$ gms. per litre. Hence, by the Distribution Law,

$$\frac{x}{50 - \frac{x}{5}} = \frac{3}{1},$$

$$x = 93.75.$$

The amount extracted is thus 18.75 gms., leaving unextracted 31.25 gms.

Let x_1 be the concentration in grams per litre in the ether layer in the second extraction. The weight extracted will be $x_1/5$ gms., leaving in the aqueous layer $(31.25 - \frac{x_1}{5})$ gms. per litre. Hence,

$$\frac{x_1}{31.25 - \frac{x_1}{5}} = \frac{3}{1},$$

$$x_1 = 58.6 \text{ gms.}$$

The amount extracted is 11.7 gms., leaving unextracted 19.55 gms.

In the third extraction, if x_2 is the concentration in grams per litre in the ether layer, by similar reasoning to the above,

$$\frac{x_2}{19.55 - \frac{x_2}{5}} = \frac{3}{1},$$

$$x_2 = 36.6 \text{ gms.}$$

The amount extracted is 7.3 gms., leaving unextracted 12.25 gms.

By similar calculation, the amount extracted in the fourth extraction is 4.52 gms., leaving unextracted 7.73 gms., and in the final extraction the amount extracted is 2.8 gms., leaving unextracted, as a result of the whole series of operations, 4.93 gms.

It is obvious from this calculation that it is considerably better to use the extracting solvent in small portions.

Using the formula

$$x_n = x_0 \left[\frac{KW}{KW + L} \right]^n,$$

we have, $x_0 = 50$, $K = 0.33$, $W = 1,000$, $L = 200$, $n = 5$. Hence,

$$x_n = 50 \left[\frac{333.3}{533.3} \right]^5 \\ = 4.76 \text{ gms.}$$

This value differs slightly from that derived by taking all the steps

separately, because in the former, approximations have been used in certain stages of the calculation.

In extraction from water, the greater the distribution coefficient, the more rapidly can the substance be extracted from the aqueous phase. It is frequently possible to increase the distribution coefficient artificially by making the substance less soluble in the aqueous phase. This can be done by adding some substance which depresses the electrolytic dissociation of the compound being extracted (§ 336). Thus, suppose that an organic acid, which ionises to a certain extent in aqueous solution, is to be extracted with ether. If a strong inorganic acid is added to the solution, the hydrogen ion concentration is increased, and the ionisation of the organic acid is reduced. In the solution there will now be a greater amount of undissociated acid, and hence the amount extracted will be greater, the ionised acid not being extracted by ether. An organic base can best be extracted in the presence of a strong inorganic base. The addition of salts will also frequently lower the solubility of an organic compound in water (salting-out effect), and thus increase the distribution coefficient.

263. Recrystallisation.—A method of purification frequently adopted is to make use of the different solubilities of the pure substance and the impurity. The impure substance is dissolved in a solvent particularly chosen for the purpose, and then by lowering the temperature, or removing some of the solvent by evaporation, the less soluble, or more abundant, substance crystallises out. Suppose we have a substance containing an impurity. Enough solvent is added completely to dissolve the substance, and if too much is taken the solvent is evaporated until crystals appear. Or, the solvent may be added hot, and when it cools crystals will come down. Now, when crystals just appear, the solution will be saturated with respect to the pure substance, but not with respect to the impurity, for the concentration of this is much smaller. Consequently, the pure substance only crystallises out, until the solution becomes saturated with respect to the impurity. Of course, the crystals which are taken from the solution will contain a small amount of the mother liquor, which will be a concentrated solution containing the impurity, and so there is bound to be a small amount of impurity on, but not in, the crystals. This can be partly removed by careful drying of the crystals in a centrifugal machine, but a second or third recrystallisation is usually needed to give a satisfactory degree of purity.

There is always a loss of material when a purification is carried out by means of recrystallisation, for a time is reached when the solution is saturated with respect to both pure substance and impurity. Further separation cannot then be effected. The greater the difference in solubility of the two substances in the solvent chosen, the more efficient will the process be, for the amount of the less soluble substance (the

substance required) present in a solution when it becomes saturated with the impurity will be smaller.

In manufacturing processes where recrystallisation is used, the process is not so simple as that outlined above. The temperature is carefully regulated, and various solvents are used by means of which more complete separation can be made.

F. SOLUTIONS OF SOLIDS IN SOLIDS

264. Solid Solutions.—When two substances are melted together, and the liquid cooled, it sometimes happens that instead of either component being deposited in the pure state, both substances are deposited together. This is usually the case when substances are isomorphous. The solid thus deposited is called a solid solution; for, although a mixture, it is perfectly homogeneous, just as a solution of a solid in a liquid is homogeneous.

Solid solutions are most frequently met with in alloys. Thus, silver and gold, and cobalt and nickel, mix with each other in all proportions forming solid solutions.

When one metal dissolves in another, it lowers the melting point, just as, when a salt is dissolved in a solvent, the freezing point of the solvent is lowered. Thus, if tin is dissolved in lead, the melting point of the lead is lowered. When a solid solution is heated it begins to melt, but does not all melt at once. The melting point of a pure solid is sharp, whilst that of a solid solution is not sharp, the melting taking place over a range of temperature. Thus, the composition of the liquid produced when the solid solution melts is not, at first, the composition of the solid

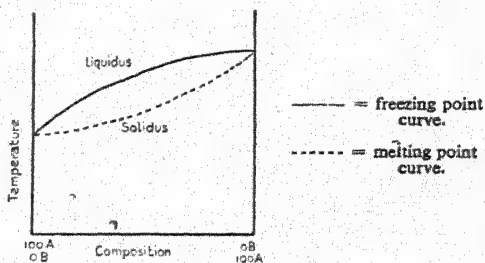


FIG. 165.

solution; only when melting is complete is this composition attained. The temperature at which solid begins to be deposited from the cooling liquid solution is usually called the freezing point of the mixture, and the temperature at which liquefaction just begins when the solid solution is heated is usually called the melting point. It is clear that

there will be two temperature-composition curves of this system, showing (a) the composition of the liquid, and (b) the composition of the solid at any given temperature. The first is called the *liquidus*, and the second the *solidus* curve (Fig. 165).

This phenomenon is met with sometimes when determining the melting point of an organic substance. Indeed, it is a usual method of recognising the presence of an impurity. If the substance is pure, the melting point is sharp; if impure, the substance melts over a range.

265. Freezing Point Curves of Solid Solutions.—There are three types of freezing point curve, just as there are three types of vapour pressure, or boiling point, curves for liquid solutions, already considered (§ 249). Indeed, the two cases are very similar.

The three freezing point composition curves are shown in Fig. 166.

In Curve I the freezing points of all mixtures lie between the freezing points of the pure components. It is rather unusual for this type of curve to be found, for it indicates ideal solution, a phenomenon rarely met with in the case of liquids, and therefore likely to be more rare in the case of solid solutions. Examples of it, however, are the solid solution of β -naphthol in naphthalene, and that of anthracene in phenanthrene.

In Curve II the freezing point curve passes through a maximum. Again, few cases of this are known.

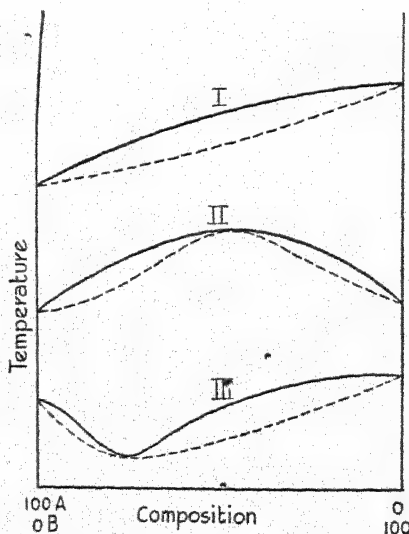


FIG. 166.

In Curve III the freezing point curve passes through a minimum, and this is the most common occurrence.

The dotted lines in Fig. 166 represent the melting point curves.

The curves given are the simplest types; more complicated cases are usually observed, though they are modifications of the simple types.

266. Fractional Crystallisation of Solid Solutions.—Exactly similar considerations govern the fractional crystallisation of solid solutions as have been applied to the question of the fractional distillation of completely miscible liquid mixtures.

Consider the liquidus-solidus curve shown in Fig. 167. Each point on the continuous line XY represents the composition of the liquid in equilibrium with the solid, the composition of the latter, at any given temperature, being indicated by the corresponding point on the dotted line. In other words, the continuous line is the freezing point curve; the dotted line the melting point curve. The example given corresponds to Curve I in the previous section.

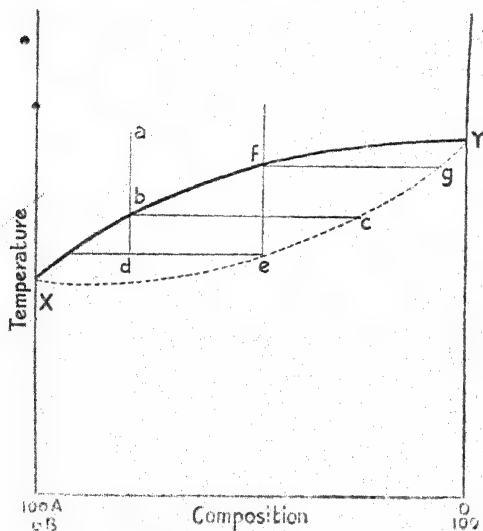


FIG. 167.

Consider a fused mixture of two substances, A and B, of the composition and temperature represented by the point a . This is cooled, and when it reaches the temperature represented by b a solid begins to separate, which will have the composition given by c . If, however, the mixture is allowed to cool to d , the solid separating has the composition given by e . Suppose the solid of this latter composition is removed from the system, and is then re-heated. It begins to melt at the temperature indicated by e , but is not entirely molten until a temperature given by the point f is reached. On cooling the liquid thus obtained, solid

begins to form at the temperature given by f , but its composition is g . It is to be noted that this solid is richer in B than the original. If the process is repeated, an almost complete separation into the two components can be effected. Theoretically, however, this would require an infinite number of operations, and so is impossible. It is possible, however, so to carry out the fractionation that the components are obtained as pure as is necessary.

As in the case of fractional distillation, it is impossible to effect complete separation when dealing with solid solutions for which the other types of freezing point-composition curve hold. A little consideration will show that if the freezing point curve has a maximum, fractional crystallisation will ultimately give a mixture having the composition corresponding to the maximum freezing point, and the liquid phase will get richer in the component which was in excess. If the freezing point curve has a minimum, the solid separating will be one of the pure components, whichever was taken in excess, and the liquid phase will approximate to the composition corresponding to the minimum freezing point.

SUGGESTIONS FOR FURTHER READING

- FINDLAY, A. "The Phase Rule and its Applications." (*Longmans*, 1940.)
ROBINSON, C. S., and GILLILAND, E. R. "The Elements of Fractional Distillation." (*New York*, 1950.)

CHAPTER XIII

DILUTE SOLUTIONS

267. Ideal Solutions.—In this chapter we shall deal with those properties of solutions which are common to all solutions, and the effect on these of altering the composition of the solution. Such properties are called *colligative properties*.

Experimental studies lead us to believe that it should be possible to express these colligative properties of solutions in terms of a simple relationship to concentration. Actually for real solutions this is only possible when the solution is dilute. Solutions, the properties of which obey simple laws, are called ideal or perfect solutions. The more dilute a solution the nearer to ideality is its behaviour.

In a systematic treatment of solutions it is necessary to define the ideal solution. This can be done thermodynamically in terms of the variation of Gibbs free energy per mol of a component of solution with the composition of the mixture. Using this definition laws such as Raoult's Law, Henry's Law and the van't Hoff expression for osmotic pressure can be deduced. However, the definition adopted here is that an ideal solution is one that obeys Raoult's Law over all compositions. An ideal solution is formed from its components without any heat being absorbed or given out and the volumes of the components are additive. Thus, if we have 100 c.c. of a solution, and add 10 c.c. of water to it, the total volume would be 110 c.c. if the solution were ideal. This, however, does not hold for any solution. There is always a slight deviation. The more dilute is a solution the more nearly does it approach ideality. That is why we shall deal in this chapter with dilute solutions only. The laws then discussed will be applicable to all dilute solutions to a close approximation; but if we include strong solutions the laws no longer hold, because these are far from being ideal. All laws of ideal solutions can be deduced from the above definition.

268. Methods of Expressing Concentrations of Solutions.—The properties to be dealt with in this chapter are determined rather by the numbers of molecules present than by the actual weights of the substances present. The method of expressing the concentration of a solution by means of the weight dissolved in a given volume, i.e., grams per litre, although it could be used, would be unnecessarily complicated. The best method is to express the concentration in gram-molecules per litre. Frequently the method of "mol-fractions" is used. If n_a is the number of gram-molecules of the substance a , and n_b that of the substance

b contained in a given solution, then the mol-fraction of a is $N_a =$

$$\frac{n_a}{n_a + n_b}, \text{ and of } b, N_b = \frac{n_b}{n_a + n_b}$$

269. Osmosis.—If a strong solution of copper sulphate is placed at the bottom of a tall cylindrical vessel, and is then carefully covered with water, so that the heavier solution is not disturbed, the two layers are, at first, more or less well defined. After some months, however, the two solutions are found to have formed a mixture, in which the two layers can no longer be discerned. This happens even though convection currents (which could cause mixture) are completely prevented by keeping the apparatus at a constant temperature throughout the experiment.

The tendency of the molecules of copper sulphate to distribute themselves uniformly through the solvent is an ordinary movement of a system towards equilibrium; that is, to a state of maximum entropy and minimum free energy. We can consider a situation in which a solution is separated from pure solvent by a membrane which is permeable to molecules of solvent but not to molecules of solute. If the pressure and temperature on both sides of the membrane are the same then the system is not in equilibrium. Equilibrium will only be attained

after all the solvent has passed through the membrane into the solution. This phenomenon is known as osmosis. We can, however, apply an excess pressure to the solution side of the membrane. When a certain pressure (dependent on the concentration of solute) is applied there will be equilibrium between solution and solvent across the membrane and no further solvent will pass through. The excess pressure necessary to bring about this equilibrium between the solvent and solution across the membrane is known as the osmotic pressure of the solution.

The phenomenon of osmosis was first observed by the Abbé Nollet, who closed the end of a tube with an animal membrane, and filled the tube with sugar solution. The tube was then placed in a beaker of water. The water entered through the membrane, diluted the sugar solution, and rose in the tube. The experiment is easily carried out with the apparatus shown in Fig. 168. The thistle funnel A has a membrane (pig's bladder) tied

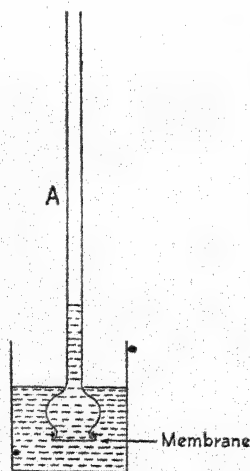


FIG. 168.—Apparatus to demonstrate the Existence of Osmotic Pressure.

over the end. It is then filled with sugar solution and placed in a beaker of distilled water. The water rises in the stem of the thistle

funnel until the hydrostatic pressure equalises the pressure driving the water in. This pressure is the osmotic pressure, and is measured by the height to which the solution will rise in the tube.

The first quantitative experiments on osmotic pressure were carried out with an apparatus like the above, using pig's bladder as the membrane. Traube showed that inorganic substances, for instance, copper ferrocyanide, $\text{Cu}_2[\text{Fe}(\text{CN})_6]$, precipitated when potassium ferrocyanide solution is added to copper sulphate solution would also act as membranes. It is necessary for a membrane of this sort to be supported in some way, and this was accomplished by producing the substance in the walls of a porous pot. It is a matter of great difficulty to get a porous pot suitable for the work. The pores must all be the same size, as otherwise certain parts of the pot have to bear more pressure than others, and the membrane is ruptured at that spot.

Osmotic pressure is of great importance in physiological processes. The walls of animal cells, and the protoplasmic lining of plant cells are imperfect semi-permeable membranes, i.e., they allow some substances to go through, e.g., water, but not others, e.g., salts, in just the same way as the pig's bladder.

If a cell containing a solution of a definite osmotic pressure be placed in a solution of less osmotic pressure, water will enter the cell in an attempt to equalise the concentrations and bring about equilibrium. The cell will swell. If, however, the reverse is the case, the cell solution having the smaller osmotic pressure, water will leave the cell and it will shrink. If it is placed in a solution of the same osmotic pressure, water neither enters nor leaves the cell, and it remains the same size. Solutions having the same osmotic pressure are called *isotonic solutions*.

270. The Experimental Determination of Osmotic Pressure.—

(a) *The Method of Pfeffer*.—A special porous pot was prepared to take the membrane in the following way: the pot was first treated with a dilute solution of potassium hydroxide, and then with a 3 per cent solution of potassium nitrate, after which it was washed out and dried. It was then filled with water, and the water forced into the pores by pressure. It was afterwards placed in a 3 per cent. solution of copper sulphate for some time to allow the salt to get well into the pores, and a solution of the same salt was placed inside the pot. The interior of the pot was washed out and quickly dried. The cell was then allowed to stand in air until the outside was just wet, when it was filled with a 3 per cent. solution of potassium ferrocyanide and again placed in the copper sulphate. After this, the cell was tested for various pressures.

In carrying out an experiment, the cell was filled with a solution, usually of sugar, of which the osmotic pressure was required. A mercury manometer was fixed to the cell, and the whole was placed in water kept at a constant temperature in a large tank. Water entered the cell, and the pressure attained was measured by the manometer.

(b) *The Method of Morse and Frazer.*—Morse and Frazer improved upon Pfeffer's method in several details, although the general procedure was the same. The chief innovation was the deposition of the copper ferrocyanide membrane electrolytically, a more even deposit being thus obtained. The cell was filled with a M/10 solution of copper sulphate, and placed in a vessel containing M/10 potassium ferrocyanide, platinum electrodes being placed in both solutions. The electrodes were connected to a battery, and the copper ions were driven out of the pot, whilst ferrocyanide ions were drawn into it. Where they met, somewhere in the wall of the pot, they combined and formed the membrane.

Morse and Frazer also used great care in choosing the correct pots for high pressure work. The results obtained by these observers are the usually accepted ones. They determined the osmotic pressure of cane-sugar solutions up to 91 per cent. strength, the strongest solution giving an osmotic pressure of 273 atmospheres.

(c) *The Method of Berkeley and Hartley.*—An important change in method was used by the Earl of Berkeley and E. G. Hartley. Instead of

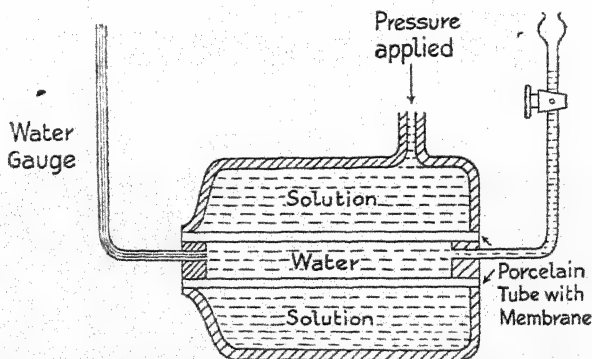


FIG. 169.—The Apparatus of Berkeley and Hartley (diagrammatic).

measuring the osmotic pressure directly, they measured the force necessary to prevent the entrance of liquid into the pot, so what they actually did was to counterbalance the osmotic pressure by an external pressure, the value of the latter giving the value of the osmotic pressure. The apparatus is represented diagrammatically in Fig. 169.

The results of the method agree with those of Morse and Frazer.

The same investigators have also used a dynamic method of measuring the osmotic pressure, by determining the rate of flow of solvent into the solution.

(d) *Methods of Comparing Osmotic Pressures.*—As has already been mentioned, the cells of plants and animals have walls composed of semi-permeable materials through which water can pass. De Vries applied this fact to the determination of relative osmotic pressures by placing

cells in the two solutions to be compared and noting how much each had to be diluted in order to give a solution of which the osmotic pressure was the same as that inside the cell.

Tammann has used an ingenious method based on the detection of the currents produced when one liquid flows into another of different density. When no currents were observed, the solutions were isotonic.

271. The Laws of Osmotic Pressure.—The following is a table of the results of Berkeley and Hartley's determination of the osmotic pressure of sucrose solutions at 0° C. In the last column, the pressure (P) has been multiplied by the volume containing one gram-molecule of the sucrose (V).

TABLE LXXI.—OSMOTIC PRESSURES OF SUCROSE SOLUTIONS
(Berkeley and Hartley)

Concentration.	Osmotic Pressure, P .	Volume containing 1 gram-mol., V .	PV .
	Atm.	Litres.	
2.02 gm./litre	0.134	169.3	22.7
10.0 „	0.66	34.2	22.6
20.0 „	1.32	17.1	22.6
45.0 „	2.97	7.60	22.6
93.75 „	6.18	3.65	22.5

It is at once seen that the product PV is constant, a relationship recalling the behaviour of a gas, and corresponding to Boyle's Law.

Since the product of the osmotic pressure and the volume containing one gram-molecule of solute is constant, the osmotic pressure divided by the concentration must be a constant. Thus, osmotic pressure is directly proportional to the concentration.

It is clear that Boyle's Law may be applied to dilute solutions if the pressure used in the equation is the osmotic pressure developed, and the concentration is the reciprocal of the volume containing a given weight of the solute.

TABLE LXXII.—EFFECT OF TEMPERATURE ON OSMOTIC PRESSURE
OF SUCROSE SOLUTIONS

t , ° C.	T , ° Abs.	Osmotic Pressure, P .	P/T .
0	273	7.085	0.02594
10	283	7.334	0.02591
20	293	7.605	0.02595
25	298	7.729	0.02594

It is remarkable that the effect of temperature on osmotic pressure is also similar to the effect of temperature on the pressure of a gas. The pressure is proportional to the absolute temperature. The table below shows the variation of the osmotic pressure of sucrose solutions with temperature according to observations by Morse and Frazer.

As the osmotic pressure of a solution is both proportional to the concentration, and to the absolute temperature, an expression such as

$$PV = KT$$

must govern the combined effect of these variables. K is a constant.

Using the data that have been obtained experimentally, the value of K may be calculated. Taking the results for a concentration of 10 gm./litre, we see from Table LXXI that the value of the osmotic pressure is 0.66 atmos. The volume containing one gram-molecule is 34.2 litres, and the temperature is 0°C ., i.e., 273°Abs .

Inserting these in the equation, we have

$$PV = KT,$$

$$0.66 \times 34.2 = K \times 273,$$

$$K = \frac{0.66 \times 34.2}{273} = 0.0824 \text{ litre-atmos. per degree.}$$

This is in good agreement with the gas constant R , which on the same system of units is 0.0821 litre-atmos. per degree (§ 122).

There are, then, clearly marked relationships between osmotic pressure and gas pressure. The same laws govern both. This can be put into a statement as follows: *The osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it were a gas at the same temperature, and occupying the same volume as the solution.*

The first to arrive at this relationship was van't Hoff, making use of Pfeffer's observations. Whilst this law is true for non-electrolytes, such as sugar and other organic substances, it does not hold for electrolytes, which give higher values for the osmotic pressure than required by this theory. The reasons for the deviation of electrolytes from the laws of dilute solutions will be taken up in greater detail later (§ 321).

272. Determination of Molecular Weights of Substances in Solution by means of Osmotic Pressure.—Since we know that osmotic pressure is related to the volume (V) of a solution containing one gram-molecule of a substance by the relationship

$$PV = 0.0821 T$$

when P is measured in atmospheres, V in litres, and T in degrees Absolute, it is clear that if we measure P and T we can find V .

To determine the molecular weight of a substance in solution by the osmotic pressure method, the osmotic pressure of a solution of the substance of known concentration is determined at a definite temperature. Inserting the values of P and T in the above equation, the volume

of solution containing one gram-molecule of the solute is obtained. Since the weight of solute dissolved in a given volume of solvent is known, the molecular weight is easily calculated.

The method is not frequently employed owing to the many difficulties attendant upon osmotic pressure measurement.

273. Numerical Examples.—Some numerical examples will make the method of calculation quite clear.

(1) Ten grams of a substance were dissolved in 250 c.c. of water, and the osmotic pressure of the solution was found to be 600 mm. of mercury at 15° C. Find the molecular weight of the substance.

Let M be the molecular weight of the substance. Then 10 gms. correspond to $\frac{10}{M}$ gram-molecules. This is dissolved in 250 c.c. of water.

Hence, 1 gram-molecule is dissolved in 25 M c.c. = 0.025 M litres.

This is V . $P = 600$ mm. = $\frac{600}{760}$ atmos. $T = 288^\circ$ Abs. Substituting these values in the equation, we have

$$PV = 0.0821 T,$$

$$\frac{60}{76} \cdot 0.025 M = 0.0821 \times 288,$$

$$\therefore M = \frac{76 \times 0.0821 \times 288}{60 \times 0.025},$$

$$= 1197.6.$$

(2) A substance of molecular weight 286 was used in an osmotic pressure experiment. A solution containing 10.3 gms. of the substance in 100 c.c. of water was made up. What osmotic pressure should the solution exert at 20° C. ?

Let P be the osmotic pressure. From the data given,

$$V = \frac{28.6}{10.3} \text{ litres.}$$

$$T = 293^\circ \text{ Abs.}$$

Substituting in the equation

$$PV = RT$$

$$P \times \frac{28.6}{10.3} = 0.0821 \times 293,$$

$$P = \frac{10.3 \times 0.0821 \times 293}{28.6} \text{ atmos.}$$

$$= 8.662 \text{ atmos.}$$

274. Theories of Osmotic Pressure and Semi-permeability.—Whilst the facts of osmotic pressure and the laws governing it are known, we are still a long way from knowing the cause of this phenomenon. Several theories have been put forward, none of which provides a

perfectly satisfactory explanation, and it seems that until a more complete theory of the liquid state is developed a satisfactory theory of osmotic pressure and of semi-permeability will not be possible.

Traube considered the semi-permeable membrane to be a sort of molecular sieve, which would allow small molecules of the solvent to pass through, but which stopped the progress of the larger solute molecules. This theory was of course only applicable to certain cases, for examples are known where the molecule of the solute must be smaller than that of the solvent, and yet the membrane still acts as a semi-permeable one.

Another theory which was put forward by Bigelow assumes that the membrane acts like a set of very fine capillary tubes, and that the process of semi-permeability is intimately connected with capillarity.

Armstrong proposed a chemical theory whereby the solvent was supposed to form a kind of loose chemical compound with the membrane, and was later split off again. There is little evidence for the truth of this view.

The theory of preferential solubility, which states that one of the substances, in this case the solvent, dissolves in the membrane, diffuses through it, and is given off again at the other side, seems to be the most generally applicable. It is supported by the experiment already quoted (§ 226) in connection with the proof of Dalton's Law of Partial Pressures, in which the hydrogen in a mixture of nitrogen and hydrogen is separated by passing the mixture through a heated palladium box. Without going

into great detail, we may say that the hydrogen dissolves in the palladium, diffuses through it, and is given off again at the other side. This gives quite a reasonable picture of what might be happening in osmosis through a semi-permeable membrane.

There are two outstanding theories of osmosis. The first is the kinetic theory, in which osmotic pressure, like gas pressure, is supposed to be due to the bombardment of the molecules of solute on the membrane. The number of

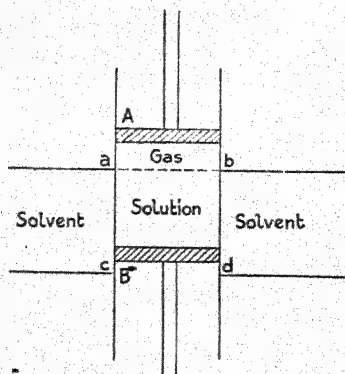


FIG. 170.

collisions of the solvent with the wall will be less on the side of the solution than on that of the solvent, and the latter therefore flows through in an attempt to make the number equal.

The other theory is the hydrostatic theory. The entrance of solvent into the solution is supposed to be due to the existence of an attractive force of the solvent for the solute. This might be due to variation of surface tension.

275. Thermodynamic Proof of the Identity of the Gas and Osmotic Pressure Laws.—This proof was originally due to Rayleigh, though it is usually associated with the name of van't Hoff. Consider a reversible cyclic process (§ 106), carried out at a temperature T° Abs.

Suppose that we have a gas at pressure p in equilibrium with its solution of osmotic pressure P . ab is a semi-permeable membrane allowing gas to pass through, but not liquid, and ac and bd , the wall of the cylinder, is also semi-permeable, allowing the solvent, but not the gas, to pass through. The pistons, A and B, are not permeable.

Stage I.—Move the pistons A and B up, so that a volume v equal to the volume occupied by one gram-molecule of the gas at pressure p is transferred through the membrane ab from the solution to the gas side. A will move up through a volume v , but B moves up through a volume V , which is equal to the volume of solution in which one gram-molecule is dissolved.

The amount of solvent corresponding to the volume of solution transferred passes through the wall ac and bd . The maximum amount of work done in the movement of the upper piston is pv , and in that of the lower PV . In the former the work is done *by* the system, in the latter *on* the system. Hence, the net work done is $pv - PV$.

Stage II.—The volume of gas, thus passed through, must be restored to the solution by a reversible and isothermal path in order to obtain the maximum amount of work. This is accomplished in this and the succeeding two stages.

The volume v of gas separated from the system is allowed to expand isothermally and reversibly to a practically infinite volume. The maximum work done in this process is

$$\int_v^{v_\infty} p dv = \int_v^{v_\infty} \frac{RT}{v} dv = RT \log_e \frac{v_\infty}{v}.$$

Stage III.—The gas is now brought into contact with a volume V of the solvent. It dissolves infinitely slowly, because it is infinitely dilute. If, however, the gas is gradually compressed with a frictionless piston, it will dissolve. Let p_1 be the pressure applied. Then the work done on the system is

$$-\int_0^{v_\infty} p_1 dv_1.$$

To evaluate the integral, we must consider the question as follows: When one gram-molecule of gas has dissolved the pressure on the piston must be equal to p , so, assuming the accuracy of Henry's Law, $\frac{p_1}{p}$ gram-

molecules will dissolve at pressure p_1 , leaving $1 - \frac{p_1}{p}$ gram-molecules undissolved.

$$\therefore p_1 v_1 = \left(1 - \frac{p_1}{p}\right) RT,$$

$$\therefore p_1 = \frac{RT}{v + v_1},$$

$$\begin{aligned} \therefore - \int_{v_1=0}^{v_1=v_\infty} p_1 dv_1 &= - RT \left[\log_e (v + v_1) \right]_{v_1=0}^{v_1=v_\infty} \\ &= - RT \log_e \frac{v_\infty}{v}. \end{aligned}$$

since v is negligible compared with v_∞ .

Stage IV.—This volume of solution must be returned to the original solution, a process which involves no work. Since we are here dealing with an isothermal and reversible cycle, the total amount of work done in it must be zero. Hence,

$$pv - PV + RT \log \frac{v_\infty}{v} - RT \log \frac{v_\infty}{v} = 0,$$

$$\therefore pv = PV.$$

By the gas laws

$$pv = RT.$$

Hence,

$$PV = RT,$$

so that osmotic pressure obeys the gas laws.

276. Raoult's Law of Vapour Pressure Lowering.—It has been known for some time that a solution of a salt boils at a higher temperature than the pure solvent. This means, of course, that the vapour pressure of a solution is less than that of the pure solvent. Gay-Lussac was among the first to investigate this lowering of vapour pressure, and he found that the vapour pressure of a solution of sodium chloride, of specific gravity 1.096, was 0.9 of that of pure water. He failed, however, to discover any law underlying the phenomenon.

Von Babo (1848-49) carried out numerous experiments on the vapour pressure of salt solutions, but discovered only that the lowering of vapour pressure and the concentration of the salt were connected by a complicated geometrical series. The work was taken up by Wüllner, in 1856, who was the first to discover the simple law at the basis of this phenomenon. He used aqueous solutions and came to the conclusion that "the diminution of the vapour pressure of water caused by substances dissolved therein, which substances do not themselves exert any noticeable pressure at the temperature of the experiment is proportional to the quantity of the substance in the solution".

In 1887, Raoult extended the work to cover other solvents besides water, and discovered the connection between the lowering of vapour pressure and the molecular weights of the solute and solvent. He stated

that "the lowerings of vapour pressures of solutions in different solvents are equal when the proportion of the number of molecules of the dissolved substance to the number of molecules of the solvent is the same". Raoult used twelve different solvents, and dissolved many substances in them, finding the relative lowering of vapour pressure for one molecule of each substance in 100 molecules of solvent. This was constant.

Combining the statement of Wüllner with that of Raoult, it may be said that *the vapour pressure of a solution is proportional to the mol-fraction of the solvent present in the solution* (§ 268). This is Raoult's Law of Vapour Pressure Lowering.

Suppose that the mol-fraction of solvent in a solution is n_s , then that of the solute must be $1 - n_s$. Let p_s be the vapour pressure of the solution. Raoult's Law states that

$$p_s = kn_s \quad (1)$$

where k is a constant.

If p_o is the vapour pressure of the pure solvent,

$$p_o = k \quad (2)$$

since, in the pure solvent, $n_s = 1$.

Hence, from equations (1) and (2),

$$p_s = p_o n_s \quad (3)$$

Now, from equations (1) and (3), a more convenient mathematical expression of Raoult's Law may be derived. We have

$$\begin{aligned} \frac{p_o - p_s}{p_o} &= 1 - n_s \\ &= 1 - \frac{\text{number of molecules of solvent}}{\text{total number of molecules in solution}} \\ \therefore \frac{p_o - p_s}{p_o} &= \frac{n}{N + n} \end{aligned}$$

where n is the number of molecules of solute, and N is the number of molecules of solvent.

The law holds only for perfect solutions. For other solutions deviations of a serious nature occur. If we are dealing with perfect solutions, we may plot the vapour pressure against the composition, and shall obtain curves of the type shown in Fig. 171. The vapour pressures of the two components are additive (Dalton's Law, § 225), so that a straight line CD is obtained upon which the total vapour pressure of the solution will lie. When a solid is dissolved in a liquid, the vapour pressure of the solid is extremely small, and hence the vapour pressure of the mixture will be practically that of the solvent. This is shown in Fig. 171.

The vapour pressure curves of mixtures of two liquids have already been dealt with (§ 249). It will be remembered that these were of three distinct types, (a) a straight line (or a line showing neither a maximum

nor a minimum), (b) a curve showing a minimum, and (c) a curve showing a maximum. Raoult's Law would hold for liquid mixtures, if such mixtures were perfect solutions (§ 267). Actually, only those mixtures which give the straight line vapour pressure curve obey Raoult's Law. The existence of maxima and minima in the curves indicates that Raoult's Law is not being obeyed.

In the case of solutions of solid non-electrolytes, Raoult's Law is of more or less general application. A solid contributes a negligible amount to the total vapour pressure, whereas, with liquids, the vapour pressures of the two components are of the same order, and deviations will be more marked.

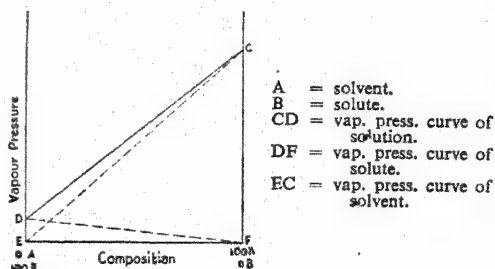


FIG. 171.—Vapour Pressure-Composition Curves for Solutions. The curves refer to one particular temperature.

277. Derivation of Raoult's Law.—Raoult's Law may be derived theoretically from the Distribution Law (§ 261). Consider the distribution of molecules of the vapour between the gaseous and liquid phases. Let N be the number of molecules of pure solvent, and n the number of molecules of solute added. The molar concentration of the solvent before the solution is made is $\frac{N}{N} (= 1)$; afterwards it is $\frac{N}{N + n}$.

Let C_o be the concentration of molecules in the gaseous phase over the pure solvent, and C the concentration of gas molecules over the solution. By the Distribution Law, the ratio of the concentrations of the same molecular species in the gaseous and liquid phases is constant. Hence,

$$\begin{aligned}\frac{C_o}{N} &= \frac{C}{N + n} = K, \\ \therefore \frac{C_o}{C} &= \frac{N + n}{N}, \\ \therefore \frac{C_o - C}{C_o} &= \frac{n}{N + n}.\end{aligned}$$

Since the concentrations of molecules in the gaseous phase are proportional to the pressure,

$$\frac{p_o - p_s}{p_o} = \frac{n}{N + n},$$

where p_o is the vapour pressure of the solvent, and p_s that of the solution. This is the mathematical expression of Raoult's Law.

278. Connection between Vapour Pressure Lowering and Osmotic Pressure.—As has been already stated, there is a definite connection between osmotic pressure and all the other colligative properties of solutions. It is the purpose of this section to derive the mathematical relationship between the osmotic pressure and the vapour pressure of a solution.

There are several methods of doing this, but the simplest is that given below.

Consider a tube, closed by a semi-permeable membrane and containing a solution, immersed in a vessel containing the pure solvent. The whole arrangement is placed under a bell-jar, which is evacuated. The osmotic pressure of the solution is measured by the height h , to which the liquid rises in the tube.

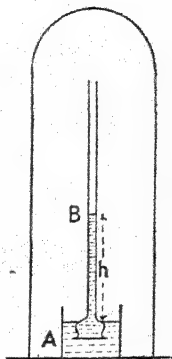


FIG. 172.

Consider the vapour pressure of the solution at B, calling it p' . This must be equal to the pressure of the vapour of the solvent at B, otherwise there would be a distillation process taking place at B. If the vapour pressure of the solution were less than that of the solvent at B, some of the solvent would condense on the solution, which would become more dilute until the vapour pressures were equalised. Conversely, if the vapour pressure of the solution were greater than that of the solvent at B, distillation would go on from the solution, and more solvent would be drawn through the membrane. In either case there would be a continuous flow of liquid up or down the tube, and equilibrium would not be established.

Now what is the vapour pressure of the solvent at B? It will be different from that at the surface of the liquid by an amount equal to the pressure of a column of the vapour of height h . Thus, if p is the vapour pressure of the pure solvent,

$$p - p' = hd,$$

where d is the density of the vapour.

We now have to find the density of the vapour. Let the molecular weight of the solvent be M . The volume occupied by M gms. of vapour at pressure p and at temperature T is

$$V = \frac{RT}{p}.$$

The density of the vapour is, then,

$$d = \frac{M}{V} = \frac{Mp}{RT}$$

Assuming that the density of the dilute solution is equal to that of the solvent s , the osmotic pressure P is given by

Hence,

$$P = \frac{hs}{s} = \frac{Mp}{RT}$$

$$p - p' = \frac{P}{s} = \frac{Mp}{sRT}, \text{ or } \frac{p - p'}{p} = \frac{MP}{sRT}$$

We can derive Raoult's equation from this statement as follows: If V' is the volume of solvent containing one gram-molecule of the solute,

$$P = n \frac{RT}{V'}$$

But

$$V' = \frac{NM}{s}, \text{ where } N = \text{number of gram-mols. of solvent.}$$

Hence,

$$P = \frac{nsRT}{NM}$$

Substituting in the equation above, we have

$$\frac{p - p'}{p} = \frac{M}{s \cdot RT} \cdot \frac{nsRT}{NM} = \frac{n}{N}$$

which is a modified form of Raoult's Law, in which n , which is small compared with N , since the solution is dilute, is neglected in the denominator.

279. Use of Raoult's Law in the Determination of Molecular Weights.—It is clear that if the lowering of the vapour pressure of a solvent brought about by dissolving a known weight of solute in a given weight of the solvent is known, its molecular concentration can be determined. Knowing the weight of substance and the volume of solvent in which it is dissolved, it is then an easy matter to calculate the molecular weight.

280. Numerical Examples.—Some examples will make this clear.

(1) The vapour pressure of water is 92 mm., at 50° C. 18.1 gms. of urea are dissolved in 100 gms. of water, and reduce the vapour pressure by 5 mm. Calculate the molecular weight of urea.

The number of gram-molecules of water present is 100/18. That of urea is 18.1/ M , where M is the required molecular weight. Raoult's Law states

$$\frac{p_0 - p_s}{p_0} = \frac{n}{N + n}$$

Substituting the values

$$p_o - p_s = 5 \text{ mm.}, n = \frac{18.1}{M},$$

$$p_o = 92 \text{ mm.}, N = \frac{100}{18},$$

we have

$$\frac{5}{92} = \frac{\frac{18.1}{M}}{\frac{100}{18} + \frac{18.1}{M}}.$$

Inverting,

$$\frac{92}{5} = \frac{\frac{100}{18} + \frac{18.1}{M}}{\frac{18.1}{M}} = \frac{100 M}{18 \times 18.1} + 1,$$

$$\therefore M = \frac{\frac{92}{5} - 1}{\frac{1}{100}} \times 18 \times 18.1 = \frac{17.4 \times 18 \times 18.1}{100},$$

$$= 56.7.$$

The molecular weight is 56.7.

(2) At 20° C. the vapour pressure of ether is 442 mm. of mercury. When 6.1 gms. of a substance were dissolved in 50 gms. of ether, the vapour pressure fell to 410 mm. What is the molecular weight of this substance ?

Here $p_o = 442 \text{ mm.}$ $n = \frac{6.1}{M},$

$p_s = 410 \text{ mm.}$ $N = \frac{50}{74},$

since the molecular weight of ether is 74.

Substituting in the equation

$$\frac{p_o - p_s}{p_o} = \frac{n}{N + n},$$

$$\frac{32}{442} = \frac{\frac{6.1}{M}}{\frac{50}{74} + \frac{6.1}{M}},$$

$$\therefore \frac{442}{32} = \frac{50M}{6.1 \times 74} + 1,$$

$$\therefore M = 115.7.$$

The molecular weight is 115.7.

281. Experimental Determination of Vapour Pressures.—There are two types of experiments by means of which vapour pressures may be determined. The first is static, and the second dynamic in nature. In the static methods the pressure itself is directly measured. In the dynamic methods the vapour pressure is obtained by measuring some effect due to it (see also § 167).

The static method was first used by von Babo in 1848, and later by Wüllner (1856), whose work paved the way for the generalisation of Raoult. Raoult himself determined vapour pressures by the static method, preparing first a barometer with a Torricellian vacuum over the mercury, and introducing the substance, of which the vapour pressure was required, over the mercury. The depression of the mercury level, owing to the vapour pressure of the liquid, was measured. This was a direct measure of the vapour pressure. By comparing the amounts of depression caused by the pure solvent in one barometer tube, and the solution in another, the lowering could readily be obtained.

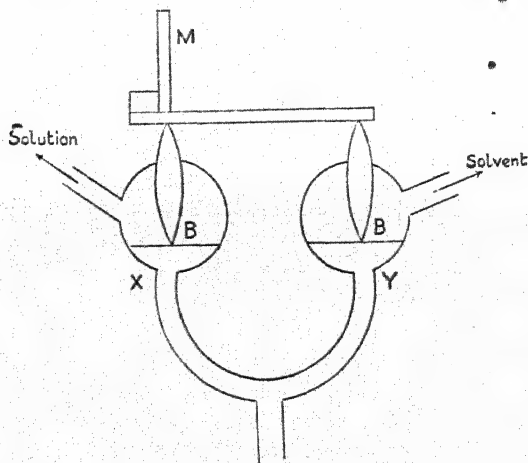


FIG. 173.—Lord Rayleigh's Differential Manometer.

Dieterici used a differential method for measuring the vapour pressure. The method depends on the determination of the difference of vapour pressure of solvent and solution. He used a glass plate connected to a quartz thread to which was attached a mirror. The glass plate was arranged so that the difference of pressure caused a movement of the plate (Fig. 174). This movement was used to twist the quartz thread, which moved the mirror. A beam of light reflected from the mirror would be deflected through twice the angle the mirror turned through. The sensitivity of the apparatus was very great, and Dieterici claimed to observe a pressure difference to an accuracy of 0.001 mm.

A similar idea to this was used by Lord Rayleigh in the construction of the differential manometer. A diagram of this apparatus is given in Fig. 173. The two limbs, X, Y, were filled with mercury. The height of the mercury in each limb was dependent upon the pressure to which each was connected. The forked manometer was tilted until the two ivory pointers, BB, just touched the level of the mercury. The angle through which the mirror M was deflected was measured by the deflection of a beam of light reflected from it. As before, the deflection of the reflected beam was twice the angle the mirror had been turned through.

This manometer was applied by Frazer and Lovelace in their experiments on the depression of vapour pressure. They obtained very accurate results for a number of solutes.

All methods of determining vapour pressures demand that the temperature be kept constant, as a slight change may alter the vapour pressure considerably.

The dynamic methods have been more extensively applied than the static ones, as they are easier to use, and can be made to yield quite accurate results.

The principle of Ostwald and Walker's dynamic method (1888) is as follows: A known volume of air is passed through the solution, and then through the pure solvent. As it passes through the solution it becomes saturated up to the vapour pressure of the solution, and the solution loses weight proportionally, the loss being determined by weighing before and after the air has passed through. As the air, already saturated to the vapour pressure of the solution, passes through the solvent it takes up a little more vapour, since the vapour pressure of the solvent is greater than that of the solution. The loss of weight of the solvent is proportional to the difference in vapour pressures of the solution and the solvent.

When the solvent is water the vapour pressure of the solvent is best obtained by passing the air, after it has been through solution and solvent, through calcium chloride tubes, which will remove all the water, and which by weighing before and after the experiment will give the total weight of water in the air, which is proportional to the vapour pressure of the solvent.

The apparatus required for this method is shown in Fig. 175. A are three wash-bottles in which is placed the solution. Then follow B, three wash-bottles containing pure solvent. These are followed by three calcium

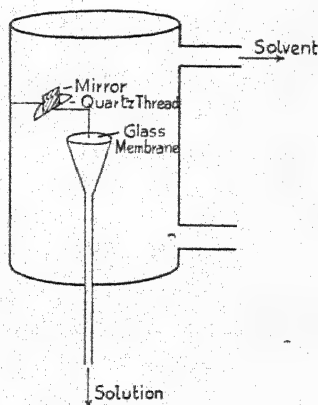


FIG. 174.—Dieterici's Apparatus.

chloride tubes. It is only necessary to weigh the wash-bottles containing the solvent before and after the experiment, and the calcium chloride tubes. The difference of weight of the former is proportional to the difference in vapour pressure ($p_o - p_s$), and that of the latter to the

vapour pressure of the solvent (p_o). We thus have $\frac{p_o - p_s}{p_o}$.

Walker applied this method to the investigation of aqueous solutions, and Will and Bredig (1889) used it for alcoholic solutions. It is obvious, when the effect of the electrolytic dissociation of salts in aqueous

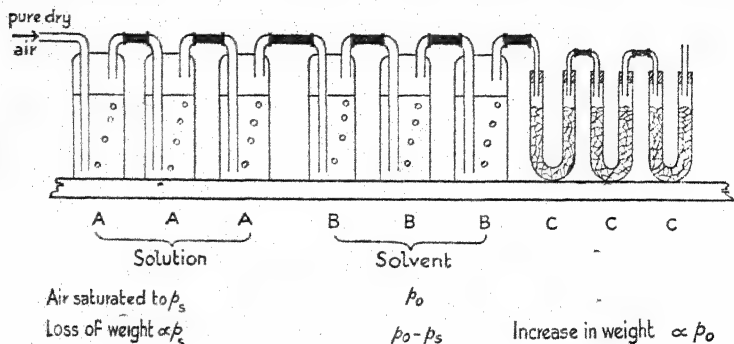


FIG. 175.—Apparatus for Ostwald and Walker's Dynamic Method.

solution on the colligative properties is considered (§ 301), that all the methods of determining molecular weights in solution based on these properties will be of much more value for organic than for inorganic substances. Many organic substances are insoluble in water but soluble in alcohol, and hence Will and Bredig's modification of the Walker method was of considerable use. Instead of absorbing the vapour of the solvent, the loss in weight of both sets of bulbs was obtained. The current of air was maintained for twenty-four hours, the flow being about 1 litre per hour.

In Menzies' method, the difference in pressure at which a pure solvent and the solution boil at the same temperature is determined. The apparatus is shown in Fig. 176. The bulb A contains the solvent, whilst the inner tube B contains the solution. This tube is provided with a scale graduated in c.c. The further inner tube C has a millimetre scale. It is first necessary to determine the zero point. This is done by connecting up the condenser D, and then half filling A with the solvent. The liquid is boiled vigorously for a few minutes to boil out any dissolved gas, and the inner vessel B is filled with the boiled-out liquid. When the liquid in the outer vessel is boiling steadily, the stopper E is removed, and the screw-clip F is partly closed. Vapour will blow through

the solvent in B. After a minute or two, the stopper is replaced loosely, and when it has warmed up it is fully inserted and the clip F opened. The liquid is kept boiling steadily. In about five minutes the level in the inner tube will have become stationary, and a little higher than that in the surrounding vessel, owing to capillarity.

A weighed tablet of the substance to be dissolved is now added to B, and the blowing through repeated. The solution having a lower vapour pressure than the solvent, the level of the liquid in the inner tube will come to rest lower than that in the tube it surrounds. The difference of the reading of the level of the liquid in the tube C, for the solution and for the pure solvent gives the lowering of the vapour pressure in terms of millimetres of solution. The density of the solution must be known, or may be taken for rough purposes as equal to that of the solvent. The concentration of the solution is known from the reading of the volume of the solution in the inner tube.

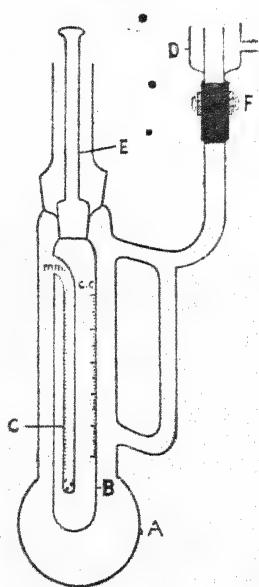


FIG. 176.—Menzies' Apparatus.

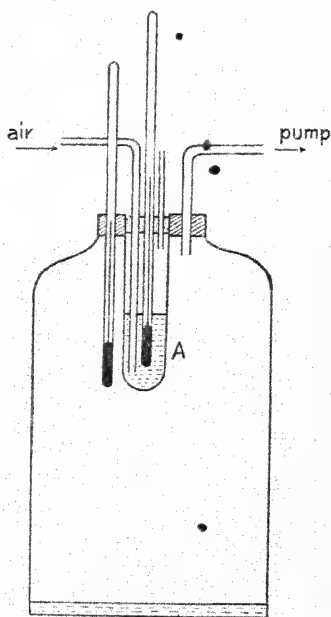


FIG. 177.—Apparatus for Cumming's Dew-point Method.

The dew-point method of Cumming is of interest, though not often used by the physical chemist. It depends upon the fact that a liquid begins to be deposited from the vapour state when the vapour is saturated. Thus dew forms from damp air when the temperature is such that the air is saturated. From a knowledge of the degree of cooling

required for the deposition of dew, the vapour pressure can be determined. The apparatus is shown in Fig. 177. A silver tube A, containing ether and bearing a thermometer graduated to 0.1°C ., and an exit and a delivery tube, is held in a cork so that its lower end is inside a bottle containing the solution. This bottle is first exhausted, and then air is blown through the ether, causing it to cool owing to rapid evaporation. This cools the vapour in the neighbourhood. The temperature at which dew begins to form is noted, and the tube is then allowed to warm up and the temperature at which the dew disappears is noted. This is repeated several times, and the mean of the results taken. This gives the dew-point. The vapour pressure of the solvent at this temperature (found from tables) is the vapour pressure of the solution at the temperature of the vapour.

282. Elevation of the Boiling Point.—Since, as has already been shown, the vapour pressure of a solution is less than that of the pure solvent, it follows that the boiling point of the solution must be higher than that of the pure solvent. This point becomes clear when the vapour pressure curves of the solvent and the solution are considered (Fig. 178). The curves AB and CD represent the variation of vapour pressure of the solvent and solution respectively with temperature. The boiling point is the temperature at which the vapour pressure of the liquid is equal to the superimposed pressure. Let P represent the superimposed pressure. Then T and T_1 will represent the boiling points of the pure solvent and the solution respectively. It is obvious that T_1 is greater than T. If, then, we measure the boiling point of a solution, we should be able to discover the molecular weight of the solute. Indeed, the determination of the boiling point of the solution under atmospheric

pressure is only another way of determining its vapour pressure.

It is usually much more convenient to determine a boiling point than to determine a vapour pressure, so the determination of the elevation of the boiling point is an exceedingly important method of determining molecular weights in solution.

It follows from Raoult's Law (§ 276) that equimolecular weights of different substances will increase the boiling point of a solvent by the same amount, since they depress the vapour pressure by the

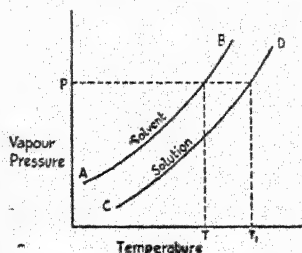


FIG. 178.—Vapour Pressure-Temperature Curves for the Solvent and Solution.

same amount. The elevation of the boiling point of a solvent caused by the solution of one gram-molecule of any substance in, say, 100 gms. of it, will therefore be a constant for that solvent. The values of these constants for the solvents most frequently used are given in Table on p. 483.

TABLE LXXIII.—MOLECULAR ELEVATION (per 100 gms. solvent).

Solvent.	K . °C.	K calc. $\frac{0.027^2}{L}$. °C.
Water . . .	5.2°	5.15°
Chloroform . . .	38.8°	38.0°
Ether . . .	21.1°	20.9°
Acetone . . .	17.2°	17.2°
Benzene . . .	25.7°	26.1°
Ethyl alcohol . . .	11.5°	11.9°

Suppose that a solution is made containing w gms. of a solvent, and W gms. of solute of unknown molecular weight M . Let the elevation of the boiling point be T° C. Now, one gram-molecular weight of any substance, dissolved in 100 gms. of the solvent, raises the boiling point by the same amount, K° C. In the solution under consideration there are W gms. of solute dissolved in w gms. of solvent. In 100 gms. of solvent there would be $\frac{100W}{w}$ gms. of solute. This raises the boiling point T° C.

The weight which will raise the boiling point by K° C. is the molecular weight.

Hence,
$$M = \frac{100WK}{wT}$$

The value of K is sometimes given for the elevation of the boiling point produced when one gram-molecule of a solute is dissolved in 1,000 gms. of solvent (instead of 100 gms. as given in the above Table). These values would be one-tenth of those given above.

283. Experimental Determination of Elevation of the Boiling Point.—(a) *Beckmann's Method.*—The method of Beckmann is the oldest of the methods used. It has been improved upon in several ways, to be described later.

The apparatus is shown in Fig. 179. A weighed amount of the pure solvent, say 25 gms., is boiled in the boiling tube A, which has a piece of platinum wire sealed through the bottom, and may also be partly filled with glass beads or garnets. The purpose of these is to prevent superheating, which is the chief source of error in the method. The point of the wire, and the beads, help to break up the bubbles of vapour, and thus prevent any superheating. This boiling tube is provided with a coiled air condenser which returns the liquid to the tube as it vaporises. If this were not used, the strength of the solution would vary throughout the determination, and no satisfactory result could be obtained.

The tube is not heated directly, but is surrounded by a heating vessel B, in which some of the same solvent is boiled. This, too, is provided with a reflux condenser, the object in this case being merely to avoid waste of the liquid. The whole apparatus is heated on an asbestos

box C, which is provided with chimneys, s, s , for promotion of currents. The boiling tube itself rests on two asbestos rings, h_1 and h_2 . The whole purpose of this is to prevent any direct heating by the flame in order to avoid superheating.

Having determined the boiling point of the pure solvent, a weighed pellet of the substance under examination is dropped into the liquid through the side tube, and the tube is again heated. The boiling point is again found. The experiment may be repeated by the addition of a fresh pellet of the substance, and noting the further rise in the boiling point.

To obtain accurate results with liquids for which the molecular elevation is small, it is necessary to use a very sensitive thermometer. Such an instrument was devised by Beckmann for this purpose. It does not read the absolute boiling points of the liquids, but merely the difference in temperature of the boiling points of the pure solvent and of the solution. This is all that is required in the calculation. It

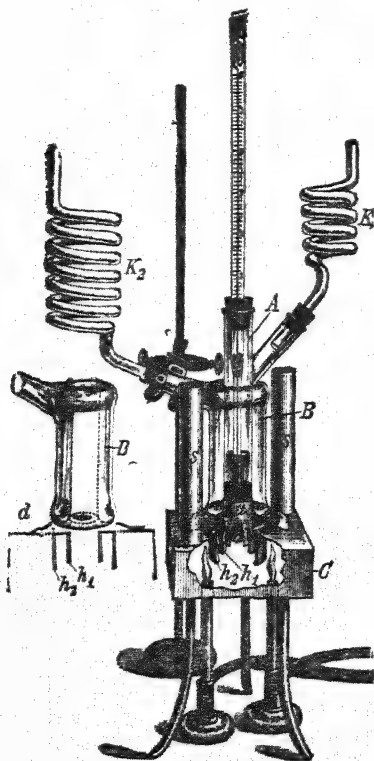


FIG. 179.—Beckmann's Boiling-point Apparatus.

[By permission of Messrs. Baird and Tatlock (London) Ltd.]

consists of a large bulb connected to a very fine capillary tube, with a bulb at the top which can accommodate excess mercury. If the thermometer is required for measuring comparatively low boiling points, it is necessary to get most of the mercury up into the top reservoir and detach it from the main thread. In this way the mercury may be made to appear on the scale at any desired temperature. This operation is known as "setting" the Beckmann thermometer. For further details, the practical text-books should be consulted.

In more modern forms of the apparatus, electrical methods of heating are used.

(b) *The Landsberger Method.*—This differs from Beckmann's method in that the solution is heated to the boiling point by passing into it the vapour of the pure solvent. Since, when the latter condenses, it gives up its latent heat, the liquid may be boiled by this means. The advantage of this process is that there is no danger of superheating. The apparatus is shown in Fig. 180.

The conical flask A contains the pure solvent. A delivery tube leads from it into a tube B graduated in c.c.'s. Towards the top of this tube there is a hole which communicates with the outer vessel C. A condenser is attached at D. A thermometer also passes into the tube B. First, a small quantity of the pure solvent is put into B, and the vapour of the solvent is blown into it until the temperature indicated by the thermometer remains constant.

This temperature is noted. It is the boiling point of the pure solvent. Now a weighed amount of the substance under test is added to B, and the passage of the vapour is continued until the temperature is again constant. This is the boiling point of the solution. The volume of the solution is noted. Knowing the density of the solvent, the mass of the solvent present in the solution, assuming the solute to occupy no volume, can be found. All the data necessary to enable the calculation of the molecular weight to be made have now been obtained.

(c) *Cottrell's Method.*—In Cottrell's apparatus an inverted funnel tube is placed in the boiling tube, which collects bubbles of vapour from a piece of porous pot in the liquid and pumps the vapour over the bulb of a thermometer, together with a stream of the boiling liquid. In this way it is ensured that the temperature indicated by the thermometer is more nearly the accurate boiling point of the liquid. The volume of solvent used is taken, and the mass of substance dissolved is known, so that the molecular weight can be calculated from a knowledge of the two boiling points. Note that in this method the bulb of the thermometer does not dip into the liquid.

(d) *Svientoslawski's Method.*—This is similar in principle to Cottrell's method in that the vapour of the liquid and a stream of boiling liquid are pumped over the thermometer bulb, but it has the advantage that

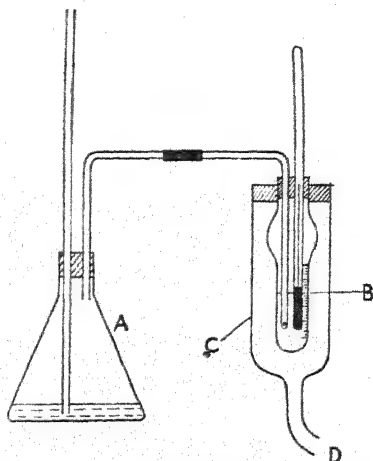


FIG. 180.—Apparatus for the Landsberger Boiling-point Method. (The small hole at the top of B cannot be shown in the figure.)

the thermometer is removed from the neighbourhood of the flame, and there is little risk of superheating.

The apparatus is shown in Fig. 182, A is a bulb tube containing the solvent. A few garnets are placed at the bottom of A to prevent superheating. The wide tube C carries a Beckmann thermometer, and is provided with a metal cylinder D resting on glass points inside the tube, to keep any direct radiation from the flame away from the thermometer. GG is an asbestos shield which serves a similar purpose. A Liebig's condenser is attached at F to return the vapour of the solvent to the boiling-vessel. A known weight of solvent is placed in A, sufficient to cause a small quantity to enter the tube C. It is gently heated until it boils, when vapour and liquid are pumped from the jet E over the bulb of the thermometer. The temperature indicated by the thermometer is taken when it becomes constant. A weighed pellet of the substance of which the molecular weight is required is dropped down

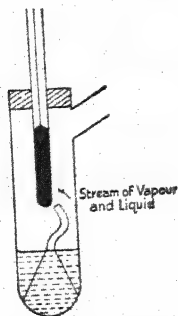


FIG. 181.—Cottrell's Apparatus.

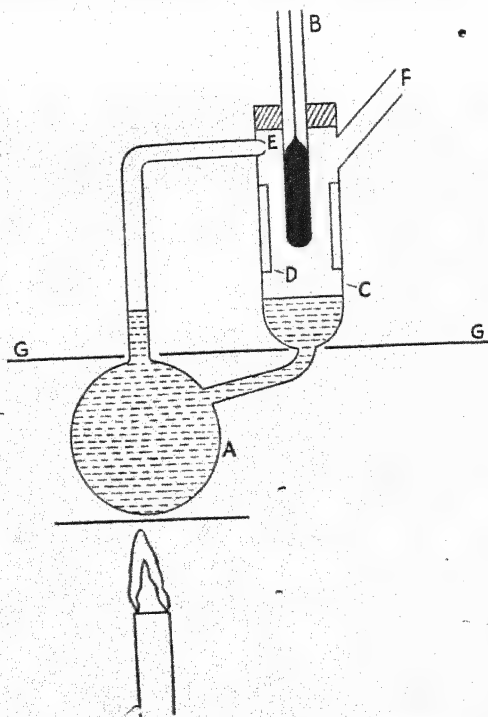


FIG. 182.—Swientoslawski's Apparatus.

the condenser and is dissolved by the solvent. The boiling point is again found. If desired, further weighed pellets of the solute may be added from time to time to provide further results.

As such great care is taken to avoid errors due to superheating, other errors should also be minimised. Thus, the amount of solvent may decrease during the experiment if the condenser is not efficient. This may be tested by weighing the apparatus and liquid before the experiment, and again afterwards (the condenser and thermometer may, of course, be omitted). After subtracting the weight of solute added from the latter reading, the weight of apparatus and solvent after the experiment is obtained. This should be the same as at first. If not, the amount of solvent lost may be regarded as having been lost uniformly throughout the course of the experiment, and if the time when the solute is added is known, the amount of solvent present then can be calculated. This correction is only of importance where the solvent is very volatile, e.g., ether.

The rate of boiling should be kept constant by not altering the flame once the liquid has begun to boil. If the rate of boiling changes, the temperature indicated by the thermometer may be slightly altered. The least error in a molecular weight determination by elevation of the boiling point by any of the above methods, is about ± 2 per cent. This error is mainly due to the difficulty in reading the temperature. Better results can be obtained by the use of resistance thermometers, but it is doubtful whether the additional complication of the apparatus is justified. Since the method is usually employed to provide confirmation of a formula, an error of 2 per cent. in the result is usually of no account.

284. Connection between Osmotic Pressure and Elevation of Boiling Point.—This can be obtained by considering a reversible process as follows: Suppose that we have a solution in a cylinder provided with a frictionless piston, which is semi-permeable, allowing solvent to be removed osmotically and reversibly. The osmotic pressure of the solution is P , and its boiling point $T + dT$, T being the boiling point of the solvent, and dT the elevation.

Stage I.—By moving the piston, remove a volume dv (the weight of which is dx) of the solvent at the boiling point of the solution $T + dT$. The work done is $-Pdv$.

Stage II.—Allow this volume of solvent, at temperature $T + dT$, to be evaporated isothermally. If L is the latent heat, the amount of work done is Ldx .

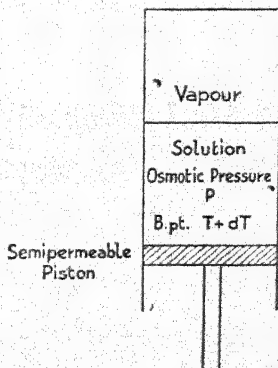


FIG. 183.—Osmotic pressure and elevation of boiling point.

Stage III.—Cool the vapour and the solution to the temperature T , adiabatically.

Stage IV.—Put the vapour in contact with the solution again at this temperature, and allow it to condense. It gives out an amount of heat $L_1 dx$, where L_1 is the latent heat at temperature T .

Stage V.—Raise the temperature adiabatically to $T + dT$. The amount of work in this process is equal and opposite to that in Stage III.

As the process is reversible, the algebraic sum of the work done in the various stages is equal to zero. Hence,

$$- Pdv + Ldx - L_1 dx = 0,$$

or

$$Pdv = Ldx - L_1 dx.$$

To find the value of the right-hand side of this expression we may apply the expression for the efficiency of a reversible cycle (§ 106). Ldx is the heat taken in at temperature $T + dT$, and $L_1 dx$ is the amount of heat given up at the lower temperature T .

The efficiency of a reversible cycle is:

$$\frac{Q_1 + Q_2}{Q_1} = \frac{T_1 - T_2}{T_1},$$

where Q_1 is the heat absorbed at temperature T_1 , and Q_2 is that given out at temperature T_2 . We thus have

$$\frac{T + dT - T}{T + dT} \cdot Ldx = Ldx - L_1 dx.$$

Hence,

$$Pdv = \frac{dT}{T + dT} \cdot Ldx.$$

Put $dx/dv = \rho$, the density of the solvent. Then we obtain,

$$P = \frac{L\rho \cdot dT}{T_1},$$

T_1 being the boiling point of the solution. This is the required relationship.

The solution is dilute, so the osmotic pressure obeys the law $P = cRT$. At temperature T_1 this becomes $P = cRT_1$, and hence

$$dT = \frac{RT_1^2 \cdot c}{L \cdot \rho},$$

which is the relationship between elevation of boiling point and concentration c .

If the density is taken as being approximately unity, the equation becomes

$$dT = \frac{RT_1^2 \cdot c}{L},$$

R is equal to 2 gm.-cals. per gram-mol. If it is assumed that one gram-molecule is dissolved in 100 gms. of solvent, then c becomes 0.01, and so

$$dT = \frac{2 \times T_1^2 \times 0.01}{L} = \frac{0.02 T_1^2}{L} = K,$$

where K is the molecular elevation. The molecular elevation can thus be calculated from a knowledge of the latent heat of evaporation of the solvent, and its boiling point on the absolute scale. It was first put forward as an empirical rule, but it is clear from the above that it has some theoretical basis.

Table LXXIII shows some values of the molecular elevation calculated for various solvents by the use of this relationship. It will be noticed that the agreement between the observed and calculated values is good.

285. Numerical Examples.—Some numerical examples will now be given in order to show exactly how data obtained from the experimental determination of the elevation of the boiling point can be used in the calculation of molecular weights.

(1) Ten gms. of a substance dissolved in 100 gms. of water raised its boiling point by 0.98°C . Calculate the molecular weight of the substance. The molecular elevation for water (100 gms.) is 5.2°C .

Since M gms. of solute (where M is its molecular weight) raise the boiling point of 100 gms. of water by 5.2°C ., the weight raising it by 0.98° will be $M \times \frac{0.98}{5.2}$. This must be equal to 10 gms.

Hence,
$$\frac{0.98M}{5.2} = 10,$$

$$M = \frac{52}{0.98},$$

$$= 53.07.$$

The molecular weight is 53.07.

(2) What elevation of the boiling point of alcohol is to be expected when 5 gms. of urea (molecular weight 60) are dissolved in 75 gms. of it? The molecular elevation of alcohol (100 gms.) is 11.5°C .

The gram-molecular weight of urea (*i.e.*, 60 gms.) would raise the boiling point of 100 gms. of alcohol by 11.5°C . Five gms. of urea would therefore elevate the boiling point of 100 gms. of alcohol by

$$\frac{11.5}{12}^\circ \text{C}.$$

As the urea is dissolved in 75 gms. alcohol, the elevation will be

$$\frac{11.5 \times 100}{12 \times 75} ^\circ\text{C.} = 1.28^\circ\text{C.}$$

286. Limitations of the Method.—In addition to the occurrence of abnormalities in the molecular weights of substances determined by this and all colligative property methods, which are to be noted later on (§ 291), it must be borne in mind that the solutes that can be used in the boiling-point method are limited to those which are not volatile. The substance dissolved must remain entirely in the liquid phase during the experiment. The method could not, then, be used to find the molecular weight of a substance like alcohol, or any other easily volatile substance.

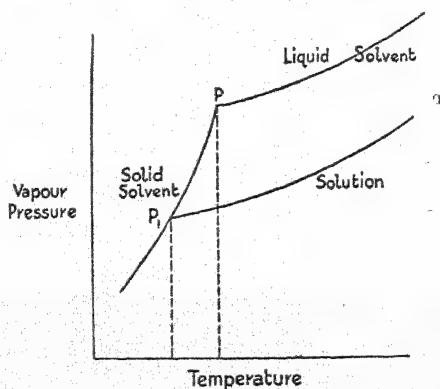


FIG. 184.

It has been pointed out by Lowry that the escape of the solute into the vapour phase corresponds to having a leaky membrane in determination of osmotic pressure.

287. Depression of the Freezing Point.—Just as lowering of the vapour pressure causes directly an elevation of the boiling point, so it directly conditions a depression of the freezing point. That this must be so follows from a consideration of the vapour pressure curves of the solid solvent, the liquid solvent, and the solution. These are shown in Fig. 184. The freezing point of the pure solvent is given by the abscissa of the point P, where the vapour pressure curves of the solid and liquid solvent intersect. If the vapour pressure of the solution is less than that of the liquid solvent, the vapour pressure curve of the solution must intersect the curve for the solid solvent at a point P₁, corresponding to a lower temperature. Equimolecular weights of substances dissolved in the same weight of a solvent depress its freezing point by the same amount.

The first experiments on the depression of the freezing point were carried out by Blagden in 1788. He noticed that the freezing point of water was depressed by the presence of dissolved salts, and that the depression was proportional to the concentration. His results were, however, overlooked, until revived by de Coppet in 1871, and by Raoult in 1882-84.

As in the case of the elevation of the boiling point, a table can be drawn up giving the molecular depression for certain solvents. The figures given (Table LXXIV) are those obtained by the dissolution of one gram-molecule in 100 gms. of the solvent. Note that the figures are not the same as for the elevation of the boiling point.

288. Experimental Determination of the Depression of the Freezing Point.—The best method is that due to Beckmann. The apparatus is shown in Fig. 185. It consists of a large outer vessel, which contains a freezing mixture. A tube, about the size of a large boiling tube, is suspended in it, and inside this is the freezing tube, which is provided with a side tube for the introduction of the weighed solid, a stirrer, and a Beckmann thermometer. The thermometer is first set so as to obtain the freezing point of the pure solvent towards the top of the scale. The apparatus is then set up and the freezing point of a known weight of the solvent is determined. The solvent is allowed to supercool a little below its freezing point, and is then stirred vigorously in order to start crystallisation. As the freezing starts the temperature rises, and remains steady at the freezing point. A weighed pellet of the substance under investigation is now added through the side tube, completely dissolved, and the freezing point of the solution found. Any considerable degree of supercooling should be avoided, since separation of much solid solvent increases the concentration of the solute.

Rast's method makes use of the fact that camphor has a very high molecular depression. One gram-molecule of a substance dissolved in 1,000 gms. of camphor produces a depression of 40° C. In this case the depression is so great that an ordinary thermometer may be used for the determination of the freezing point.

A known weight of the substance under investigation is mixed with a known weight of camphor, and the two are intimately fused together, the mass allowed to cool and then broken up. The melting point of the mixture is then determined in the usual way in a capillary tube. The melting point of pure camphor is also determined. The molecular weight

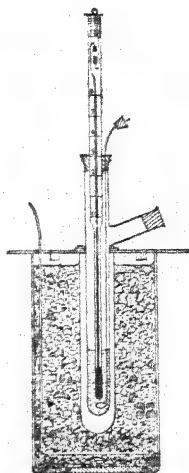


FIG. 185. — Beckmann's Freezing-point Apparatus.

is then calculated from a formula similar to that for elevation of boiling point (§ 282).

Some compounds with higher depression constants than camphor are known. They are all members of the hydroaromatic class. Pirsch (1933) has found that camphorquinone has a high constant (457° C. for 100 gms.), and has a fairly high melting point (197.2° C.), and good solvent properties. With pinene dichloride and pinene dibromide, the constants are 562° C. and 809° C. respectively. These two substances form a continuous mixed crystal system, and the depression constant is additive for these mixtures, *i.e.*, it is a function of the composition of the mixture. Bornylamine gives a molecular depression constant of 406° C., and is especially useful in determining the molecular weights of alkaloids.

TABLE LXXIV.—MOLECULAR DEPRESSION
(per 100 gms. solvent)

Solvent.	K° C.	K calc. $\frac{0.02T^2}{L}$.
Water	18.5°	18.6°
Acetic acid	39°	38.2°
Phenol	53°	50.5°
Camphor	400°	—
Naphthalene	69°	69.5°
Benzene	51.2°	50.7°
Camphor quinone	457°	—
Pinene dichloride	562°	—
Pinene dibromide	809°	—
Bornylamine	406°	—

It has the disadvantage of being very volatile at the melting point, and hence sealed melting point tubes must be used.

Raoult suggested that there might be some connection between the molecular depression and the molecular weight of the solvent, but no simple relationship has been discovered.

289. Connection between Osmotic Pressure and Depression of the Freezing Point.—By means of a thermodynamic cycle exactly similar to that used in the case of elevation of boiling point, the relationship between osmotic pressure and depression of the freezing point can be derived. The student is recommended to attempt this for himself.

The final relationship is

$$P = \frac{L\rho \cdot dT}{T_0},$$

where ρ is the density of the solvent, dT , the depression of the freezing

point, and T_0 the freezing point of the solution, and L the latent heat of fusion of the solvent. As before, we can substitute the value of the osmotic pressure and obtain the expression

$$dT = \frac{RT_0^2 \cdot c}{L_0}$$

This gives, as before,

$$K = \frac{0.02T^2}{L}$$

This enables the molecular depression, K , to be calculated if the latent heat of fusion of the substance, L , and its freezing point on the absolute scale are known.

290. Numerical Examples.—(1) Fifteen gms. of a substance dissolved in 150 gms. of water lowered its freezing point by 1.2° C. Find the molecular weight of the substance. The molecular depression for water is 18.5° C. (100 gms.).

Since 15 gms. of substance are dissolved in 150 gms. of water, 10 gms. are dissolved in 100 gms. of water.

One gram-molecule of the substance, dissolved in 100 gms. of water, depresses the freezing point by 18.5° C. Hence, if M is the molecular weight of the substance, $\frac{M \times 1.2}{18.5}$ gms. of it will depress the freezing point of water by 1.2° C. This weight must be equal to 10 gms.

$$\therefore \frac{1.2M}{18.5} = 10$$

$$M = \frac{185}{1.2} \\ = 154.2.$$

(2) A sample of pure prismatic sulphur melted initially at 119.25° C., but in the course of a few minutes the melting point fell to 114.5° C. When the sulphur had completely melted at this temperature the liquid sulphur was plunged into iced water; 3.6 per cent. of the resultant solid sulphur was then found to be insoluble in carbon disulphide. Deduce the molecular formula of the type of sulphur insoluble in carbon disulphide. The latent heat of fusion of sulphur is 9 cal. per gram. (St. Catharine's College, Cambridge, Schol., 1932.)¹

We can obtain the molecular depression of sulphur, K , from the Rule (§ 289),

$$K = \frac{0.02T^2}{L},$$

where T is the freezing point of the pure sulphur on the absolute scale and

¹ This question is quoted by permission of the Syndics of the Cambridge University Press.

L is the latent heat of fusion.

Now, $T = 119.25^\circ \text{C.} = 392.25^\circ \text{Abs.}$

and $L = 9 \text{ cal. per gram.}$

$$\therefore K = \frac{0.02 \times (392.25)^2}{9}$$

$$= 341.8^\circ \text{C.}$$

After the melting, some $S\lambda$ is formed, and the melting point is lowered 100 gms. of the mixture contain 3.6 gms. of $S\lambda$. Hence, 96.4 gms. of solvent contain 3.6 gms. of solute. The depression is $119.25^\circ - 114.5^\circ = 4.75^\circ$. Let M be the required molecular weight. Then, M gms. dissolved in 100 gms. of sulphur depress the freezing point by 341.8°C.

Hence, $\frac{M}{341.8} \times 4.75$ gms. in 100 gms. of sulphur depress the freezing point by 4.75°C. , and $\frac{M}{341.8} \times \frac{4.75 \times 100}{96.4}$ gms. in 96.4 gms. of sulphur depress the freezing point by 4.75°C.

This weight must be equal to 3.6 gms.

$$\therefore M = \frac{3.6 \times 341.8 \times 96.4}{4.75 \times 100}$$

$$= 249.8.$$

This corresponds to the formula S_8 (approximately).

291. Abnormal Molecular Weights.—Since all the properties described in this chapter are proportional not to the weight of substance dissolved, but to the molecular concentration of the solution, the effects must be due to the numbers of molecules of solute in the solution. If, then, a substance does not dissolve as single molecules, the effects will not indicate the true molecular weight of the substance as shown by the formula.

Thus, if a substance associates in the solvent, then the number of individual particles present will be half what there would be if association did not occur (assuming the association of single into double molecules). The molecular weight indicated by these methods will then be double the true molecular weight, as indicated by the formula.

Similarly, if dissociation occurs (§ 297), as it does whenever a metallic salt is dissolved in water, the number of individual particles (this time the ions) is greater than the number of molecules that would otherwise be present in the solution, and the molecular weight indicated by these methods is smaller than that derived from the formula of the substance.

Van't Hoff introduced into the osmotic pressure equation a factor i , which would include these anomalies. The osmotic pressure equation then becomes

$$PV = iRT.$$

For normal solutions $i = 1$, but for abnormal solutions the factor is obtained by dividing the experimental value for the molecular depression by the normal value. Thus, when one gram-molecule of sodium chloride is dissolved in 100 gms. of water the molecular depression is 36, whereas the value for a normal substance is 18.5. Hence, $i = 36/18.5 = 1.94$.

It is possible to calculate the degree of association or dissociation from the values of the molecular weight determined by any of these methods. Let us consider first the case of *association*. Let the degree of association be x , and n the number of molecules which come together to make the associated molecule. If 1 gram-molecule of the substance is considered, the simple molecules left will be $1 - x$ gm.-mol. The associated molecules formed will be x/n gm.-mol. Hence, the number of particles in solution will have been reduced in the ratio $1/(1 - x + x/n)$. If the molecular weight is determined by the depression of the freezing point and F_o is the observed depression, and F_c the calculated depression assuming no association, then

$$\frac{F_o}{F_c} = \frac{1 - x + \frac{x}{n}}{1}$$

$$x = \frac{F_c - F_o}{F_c \left(1 - \frac{1}{n}\right)}$$

but $\frac{M_c}{M_o} = \frac{F_o}{F_c}$, where M_c = calc. molecular weight
 M_o = observed molecular weight

$$\therefore x = \frac{M_o - M_c}{M_o \left(1 - \frac{1}{n}\right)}$$

For dissociation, let x be the degree of dissociation and n the number of ions formed from one molecule, then the actual number of particles present is $1 - x + nx$ times greater than it would be in absence of dissociation, and the ratio F_o to F_c is given by

$$\frac{F_o}{F_c} = \frac{1 - x + nx}{1}$$

$$\therefore x = \frac{M_o - M_c}{M_o(n - 1)}$$

292. Real Solutions.—Real solutions only behave ideally when they are dilute. In order to express the relationship between vapour pressure and concentration in a real solution, it is necessary to replace concentration in the various ideal relationships by activity (a). Activity is related to concentration by the equation $a = fc$ where c is the concentration and f is called the activity co-efficient. The activity co-efficient is a measure of the deviation of the solution from ideality.

In theoretical discussions of real solutions, solutions of electrolytes and non-electrolytes are treated separately. The deviations of the former are calculated mainly on the basis of the electrostatic forces between ions (see Chapter XV). For non-electrolytes, the deviations are considered in terms of solvent-solute interaction forces and in terms of differences in size of the molecules of solvent and solute.

We will now consider solutions of non-electrolytes. If f is greater than one (when concentrations are expressed as mol fractions), the deviations are called positive deviations; those for which f is less than one are called negative deviations. The vapour pressure curves for positive deviation are given in § 249, Fig. 148 (c); those for negative deviations are Fig. 148 (b).

The free energy of mixing of N_1 mols of one component with N_2 mols of another in the formation of an ideal solution at temperature T can be shown by thermodynamic methods to be

$$N_1 RT \log_e N_1 + N_2 RT \log_e N_2.$$

This mixing involves (like any other natural process) a decrease in free energy. Now $\Delta G = \Delta H - T \Delta S$. But for ideal solution formation $\Delta H = 0$ and hence $\Delta G = -T \Delta S$.

$$\therefore -\Delta S = R(N_1 \log_e N_1 + N_2 \log_e N_2)$$

For the formation of an ideal solution, the entropy increase is what would be expected from the increased randomness of the components on mixing. For positive deviations ΔG is less negative. That is the solutions mixed less readily and if the deviations are great ΔG may become positive and the liquids will be non-miscible. Curves of ΔG plotted against the composition of a mixture usually have one minimum as curve *a* in Fig. 186, but for solutions with large positive deviations from ideality there may be two minima (as curve *b* in Fig. 186). For all compositions represented on the curve by points between the minimum points A and B the solution will separate into two layers of composition equal to those at A and B. As the temperature is raised the solutions will tend to move towards ideality until the curve of ΔG against composition will become as curve *c*, Fig. 186. Here the two minima have coalesced into one and the components are now miscible over all compositions. The temperature at which this occurs is the critical solution temperature (§ 244).

For negative deviations ΔG is more negative than for ideal mixtures and the tendency for the components to mix is greater than that shown by ideal components.

In non-ideal solutions the heat of solution ΔH may be positive or negative while ΔS (the entropy of mixing) may be equal to or greater or less than the ideal value. Hildebrand has classified the various types of non-ideal solutions on the basis of the type of deviation of ΔH and ΔS from ideality. He attempted to give a theoretical account

of the behaviour of solutions in terms of intermolecular interactions. Deviations from ideality may be caused in a number of ways. For example if the sphere marked "x" in Fig. 187 is a solvent molecule surrounded by other solvent molecules there are definite intermolecular forces between "x" and its neighbours. If "x" is replaced by a solute molecule the intermolecular forces now affecting the molecule at "x"

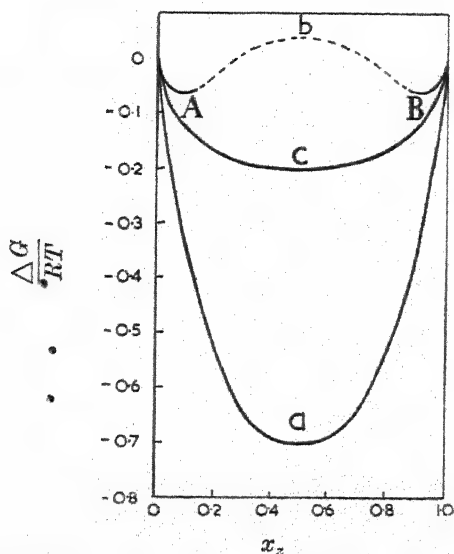


FIG. 186.—Relation between Free Energy of Mixing and Composition of a Solution.

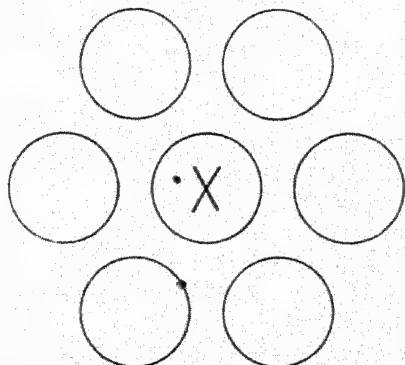


FIG. 187.—Hypothetical Distribution of Molecules in Liquid.

may be changed. This will lead to deviations from ideal behaviour. Deviations are also due to compound formation between solvent and solute (for example the formation of hydrates in aqueous solutions) and also to association of the solute or the solvent molecules.

SUGGESTIONS FOR FURTHER READING

HILDEBRAND, J. H. and SCOTT, R. L. "The Solubility of Non-Electrolytes." (*Reinhold Publishing Corpn.*, 1950.)

CHAPTER XIV

ELECTRICAL CONDUCTION IN SOLUTIONS AND METALS

293. Types of Conductor.—Fairly early in the history of electricity it was realised that solid substances fell roughly into two classes—conductors of electricity and non-conductors, or insulators. This was known before the discovery of the phenomena of voltaic electricity. When, however, Volta made his cell (1799), the conduction of electricity by liquids was investigated, and in the year after the cell was made the products of decomposition of water when the current was passed through it were being studied. It was soon discovered that most liquids, unlike solids, were decomposed by the current when it was passed through them. As soon as the current stopped, the decomposition ceased, indicating quite clearly that the decomposition was in some way bound up with the passage of the current. Also, the products appeared only at the poles, where the electricity entered or left the solution. These liquids, which undergo decomposition, were later called *electrolytes* by Faraday. He also gave names to the poles, the positive pole, at which the electricity was supposed to enter the solution, being called the *anode*, and the negative pole, where it was supposed to leave, the *cathode*.

Since that time it has been discovered that it is solutions of acids, bases and salts which undergo decomposition in this way.

All that is apparent in electrolysis is a decomposition of the solution at the electrodes. It may be pointed out that a certain minimum electromotive force must be applied to the electrodes before electrolysis will occur. This minimum voltage varies from electrolyte to electrolyte, and also depends upon the nature of the electrodes. The reason for its existence is that the products of the electrolysis in contact with the electrodes cause a back electromotive force (e.m.f.), which must be overcome before electrolysis will take place. It is called a polarisation e.m.f. The hydrogen gas in contact with the platinum electrode in the electrolysis of water causes a back e.m.f., since it acts as a voltaic cell. Where there is no polarisation, this minimum e.m.f. is no longer necessary. Thus, the smallest applied potential will bring about the electrolysis of copper sulphate between copper electrodes. In all cases there is a small amount of decomposition as soon as the e.m.f. is applied, no matter how small it is, but unless the applied e.m.f. is greater than the polarisation e.m.f. there is no further decomposition (see also § 341).

294. The Grotthus Chain Theory.—The peculiar fact that decomposition in electrolysis takes place only at the electrodes and not in the bulk of the solution was first explained by Grotthus in 1805. He supposed that the passage of the current, and the chemical changes produced by it, were due to the successive decomposition and recombination of particles of the dissolved substance. In Fig. 188 the molecules are AB, AB, etc. As soon as the electrodes are placed in the solution, these molecules are turned in the direction shown in the figure (I). Owing to the attraction of the electrodes, A is split off at one end, and the B part of the molecule finds itself free (II), so it attacks the next molecule to it, depriving it of its A portion. This goes on all along the chain until the B part of the end molecule next the electrode finds itself without any further molecules to attack, and so is liberated at the electrode opposite to that at which the A was originally set free. It will be seen from this theory that the two parts of the molecule liberated in electrolysis do not come from the same molecule, but from entirely different ones. When the B part has been liberated it is seen from the figure that the molecules are all the reverse way round to what they were

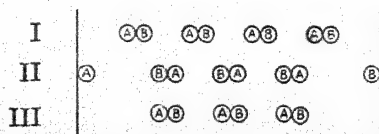


FIG. 188.—The Grotthus Chain Theory.

to start with, and so, before further decomposition takes place, they must all be turned round by the attractive force of the electrodes (III).

This theory was disproved by the fact that Ohm's Law (which states that the current (I) flowing in a circuit is proportional to the applied electromotive force (E), the ratio E/I being the resistance R) was found to apply to solutions of electrolytes, and hence all the electrical energy was used in overcoming the resistance of the solution and none in breaking up the substance into the parts A and B referred to above.

295. Faraday's Laws of Electrolysis.—The quantitative laws governing the decomposition of electrolytes by the electric current were derived by Faraday in 1834. These have been referred to already in Chapter II., but will be repeated here. Faraday gave the name "ions" to the parts into which the molecule was decomposed on solution (§ 297). His two Laws of Electrolysis are:—

(1) The amount of decomposition caused in electrolysis is proportional to the quantity of current passed.

(2) For the same quantity of electricity passed through different solutions the amount of decomposition is proportional to the equivalent of the element, or group, liberated.

Thus, if the same current is passed for the same time through solutions of copper sulphate, silver nitrate and lead nitrate, the amounts of metal deposited at the cathode are proportional to the equivalents of the metals, *i.e.*, to 31.78, 107.88 and 103.61 respectively.

The verification of these Laws is a fairly simple matter, and is dealt with in Physics.

296. The Theory of Clausius.—After the failure of the Grotthuss chain theory to account satisfactorily for all the facts of electrolysis, no further theory seems to have been put forward until that of Clausius in 1857. It is true that Faraday modified the Grotthuss theory, but not to any great extent. Clausius stated that in solution an electrolyte is invariably split into its ions, and that there is an equilibrium between the ions and the undissociated electrolyte. Only a minute proportion of the free ions was supposed to exist at any one time. The free ions were charged, and therefore travelled towards the electrodes bearing the opposite charges, and there became discharged and liberated as the ordinary products of electrolysis.

This theory was satisfactory, but there was no quantitative expression bound up with it. That was left to Arrhenius.

297. The Arrhenius Theory of Electrolytic Dissociation.—It has been mentioned (§ 291) that electrolytes give anomalous results in osmotic pressure determinations, and that van't Hoff therefore introduced the factor *i* in the expression

$$PV = iRT$$

to cover these anomalies. Similar anomalies were also found in the lowering of the vapour pressure, and depression of freezing point, and elevation of the boiling point, since all these properties are connected with osmotic pressure. Arrhenius (1887) stated that these anomalies could be accounted for if it were assumed that the dissolved substance were partly broken up into electrically charged atoms or groups, called ions, and this assumption was supported by the fact that the substances which gave the anomalous results were all of them electrolytes. Arrhenius took this view not only on the basis of abnormalities in osmotic pressure and other colligative properties, but also as a result of a great deal of work on the conductivity of solutions of electrolytes. From the results of osmotic pressure and electrical conductivity he was able to state the extent of the ionisation.

This view was also put forward by Planck in the same year, though he studied it from the point of view of thermodynamics. He was able to say that the observed abnormalities of freezing point, etc., could only be brought into harmony with thermodynamical laws if the molecules were supposed to be broken down into parts to some extent.

This theory of electrolytic dissociation has played a very great part

in the development of electrochemistry. According to this theory we must suppose that immediately an electrolyte is dissolved in water it is at least partly dissociated into its ions, which are free and moving about with random motion in the liquid. When the e.m.f. is applied, the ions are attracted towards the electrodes bearing the opposite sign, and when they reach it they are discharged and appear at the electrode in their normal condition.

This theory, when it was first put forward, met with the greatest opposition, and some of the arguments against it are worth while mentioning here. The arguments for it are given later (§ 314).

(1) In many cases the ions produced were of substances which would react with water in the ordinary state. It was argued that the sodium ion could surely not exist in the presence of water, having regard to the well-known violent action of sodium on water. Also chlorine could surely not exist in the free state in a solution of sodium chloride, since it is a green gas. But this argument arises from a misconception of the theory. The theory states that the ions of these substances, and not the substances themselves, exist in solution. The ions are the charged atoms or groups, having lost or gained electrons (§ 73). The point is very clearly brought out when we consider the difference between an ion and an atom according to the electronic theory.

(2) It was said that the affinity between the different parts of the molecule, *e.g.*, sodium and chlorine in sodium chloride, was very great, and that the mere fact of solution in water should be insufficient to break down the bond between them. It is not, however, the affinity between the atoms, but that between the ions, that is in question. It is now known that common salt is ionised even in the solid state.

(3) If there are ions in solution it was argued that it ought to be possible to separate them by diffusion. The electrical charges carried by the ions would however tend to prevent this; being equal and opposite, they would tend to keep the ions in the form in which they occur in the space lattice of the crystal. It is, however, possible to effect a slight separation by diffusion. Tolman (1911) centrifuged solutions of certain iodides, and found that the ends of the tubes containing the solution became charged oppositely, presumably owing to the heavier iodide ions being in excess at one end, and the lighter metal ions at the other.

(4) It was at first thought that all instantaneous reactions in solution were due to interaction between ions. Several such reactions between substances in non-conducting solutions were, however, discovered, and these were brought forward as arguments against the dissociation theory. It is now known that instantaneous reaction need not necessarily take place between ions, so this argument carries no weight.

Numerous other objections were put forward, and other methods of explaining the anomalies in the colligative properties were given, but

all have been shown to be of no importance. The evidence for the truth of the theory of dissociation is now so strong that it is held by every chemist.

The view of Arrhenius was that *all* electrolytes are *partly* dissociated into their ions on solution in water. It is now believed that certain substances, called *strong electrolytes*¹ (e.g., sodium chloride, hydrochloric acid, etc.), are completely dissociated in aqueous solution. The apparent degree of dissociation shown by these electrolytes is due to interionic forces. This view will be developed in § 302.

298. The Determination of the Conductivity of an Electrolyte.—The resistance of a circuit is given by Ohm's Law as the ratio of the applied voltage to the current which flows. Thus

$$E/I = R,$$

where E is the voltage in volts, I the current in amperes, and R the resistance in ohms.

In order to be able to compare the resistances of different substances, the *resistivity* is used. This is defined as *the resistance of a specimen of the material of length 1 cm., and 1 sq. cm. area of cross-section*. If l is the length of a conductor, and a its area of cross-section, and R its resistance, then it follows that

$$R = Sl/a,$$

where S is the resistivity, or specific resistance.

The *reciprocal of the resistivity* is called the *conductivity*, κ , of the material.

These definitions apply equally to electrolytes and to solids, though the matter is somewhat complicated in the case of electrolytes by the conductivity being dependent upon concentration, and therefore, to obtain comparable results for different solutions, it is necessary to compare their conductivities at equivalent concentrations.

The *equivalent conductivity* is defined as the *conductivity multiplied by the volume in c.c. containing 1 gm. equivalent of the electrolyte*. It is usually given the symbol Λ . Hence if κ is the conductivity, and V the volume containing 1 gm. equivalent,

$$\Lambda = \kappa V.$$

The *molecular conductivity* is the *conductivity multiplied by the volume in c.c. containing one gram-molecule of the electrolyte*. It is usually given the symbol μ .

Having defined the terms, it is now possible to proceed to the method

¹ Strong electrolytes are those electrolytes which do not obey Ostwald's Dilution Law (§ 318), and the class comprises most electrolytes which give good conducting solutions at moderate dilutions. This definition will be more clearly understood after reading Chapter XV.

of determining the conductivity of an electrolyte. We will suppose that we require the equivalent conductivity of a solution of common salt at 25° C. The temperature must be specified, since the resistance varies considerably with temperature.

A modification of the Wheatstone's bridge method of determining the resistance of a solid conductor is used. The solution of which the resistance is required is placed in a special cell, a common form of which is shown in Fig. 189. It is necessary that the distance between the electrodes should remain quite fixed during an experiment, yet it is desirable not to have them permanently fixed. The distance apart of the electrodes and their area of cross-section must be known, if it is desired to determine the conductivity of a substance without the use of a reference electrolyte. It is very difficult to measure these, and so it is usual to determine the resistance of a solution of potassium chloride of known con-

centration (usually $\frac{N}{10}$) in the cell, and, from the

known conductivity of this solution, to calculate the "cell constant", *i.e.*, the factor by which the observed resistance has to be multiplied to obtain the resistivity of the electrolyte.

When a current is passed through an electrolyte, polarisation of the electrodes occurs if gases are evolved during the electrolysis. The presence of the layer of gas at the electrodes causes a considerable increase in the resistance, and in conductivity measurements must be prevented. This is usually done by employing a rapidly alternating e.m.f., which, if it is symmetrical, produces no polarisation, the polarisation produced by one half of the wave being immediately neutralised by that due to the other half. As a source of the alternating current, Kohlrausch used a small induction coil, though actually this gives not pure alternating current, but a pulsating direct current, and cannot be used for very accurate work. High-frequency generators have been used, but the ordinary wireless valve is most commonly employed. It is found that the conductivity of a solution varies with the frequency of the current used, so that for very accurate work the frequency should be known. Further, to avoid polarisation, the electrodes, which are of platinum, are coated with platinum black by electrolysis a solution of platinic chloride in the cell before any experiments are done with it.

An ordinary galvanometer will not detect an alternating current. Galvanometers can be made for alternating current, but they are not, as a rule, so sensitive as direct-current instruments. Telephones are

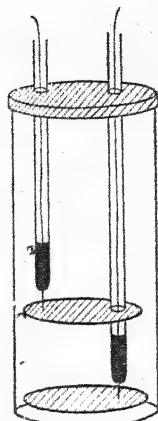


FIG. 189.—Conductivity Cell.

frequently used, sometimes in conjunction with a valve amplifier, for greater sensitivity.

The circuit is arranged as shown in Fig. 190. The sliding contact C is moved along the bridge wire AB, until the position giving minimum sound in the telephones T is obtained. The ratio of the lengths of the bridge wire is equal to the ratio of the resistances:—

$$\frac{\text{Resistance of electrolyte}}{\text{Resistance in box}} = \frac{AC}{BC}$$

In carrying out an experiment, the electrodes of the cell are first platinised by putting some platinum chloride solution into the cell, and passing the current for half-minute intervals in each direction. When the electrodes are thoroughly blackened, they are removed, and the cell and electrodes thoroughly washed with distilled water. The cell is now filled

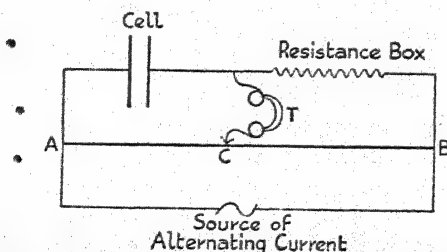


FIG. 190.—Circuit for determining Conductivity.

with distilled water, and its resistance determined. If the resistance is less than 2 to 4 megohms, the electrodes still contain soluble matter, which must be removed by further washing. The washing must be repeated until the resistance reaches the above figure. For accurate work the cell should be placed in a thermostat, the usual temperature being 25° C. The cell is now filled with a potassium chloride solution containing 0.1 gram-equivalent in 1 litre, and the resistance found. The conductivity of a *N*/10 potassium chloride solution is known (Table LXXV). The "cell constant" can now be calculated. The conductivity κ is connected with the resistance by the equation

$$\kappa = \frac{l}{aR}$$

where the symbols have the meanings given at the beginning of this paragraph. The cell constant is $\frac{l}{a}$, and is thus found by multiplying κ by R .

The cell is now thoroughly washed out, as before, filled with the solution under test, and the resistance again determined. If R' is the

resistance, k the cell constant, then κ' , the conductivity of the solution, is given by

$$\kappa' = \frac{k}{R'}$$

TABLE LXXV.—CONDUCTIVITY OF $D/10^1$ POTASSIUM CHLORIDE AT VARIOUS TEMPERATURES (Parker and Parker)

Temp., °C.	κ .
0°	0.007129
10°	0.009316
18°	0.011163
25°	0.012852

The molecular and equivalent conductivities of the solution are found by multiplying the conductivity, κ' , by the volume in c.c.s. containing one gram-molecule, and one gram-equivalent respectively.

For very accurate work, solutions should be made up with specially purified water, known as conductivity water. It is not usually satisfactory to determine the resistance of the water and subtract it from the resistance of the solution. Kohlrausch and Heydweiller (1894) prepared very pure water by distilling it forty-two times, under reduced pressure. The water had a conductivity of 0.043×10^{-6} mhos.² It is a moot point whether this value has any real significance, as, by the process of distillation, the proportion of H_2O to H_2O in water is altered, and the composition of Kohlrausch and Heydweiller's specimen is not known.

For ordinary purposes conductivity water is prepared by distilling freshly distilled water with a small amount of potassium permanganate in a retort made of resistance glass, with a condenser of block-tin, or of resistance glass. Any corks used must be covered with tin-foil. Several stills have been devised for the routine preparation of conductivity water.

To illustrate the meaning of the terms an example may be taken.

¹ The symbol $D/10$ stands for a concentration of one gram-equivalent in one cubic decimetre. The cubic decimetre is not exactly one litre, as at present defined, but is equal to 0.999973 litres. This arises from the fact that although the cubic centimetre was the original unit of volume, the litre has now been defined, not as 1,000 c.c., but as the volume of 1 kilogramme of pure, air-free water at the temperature of maximum density and under a pressure of 760 mm. This volume is not quite 1,000 c.c., but a little greater. In order to avoid confusion, many workers use the millilitre (ml.) instead of the cubic centimetre (c.c.) as a unit. Since the volume involved in our definition of equivalent conductivity is the c.c., we must use the cubic decimetre instead of the litre if very accurate results are necessary. In the experiment, as described above, it would not be necessary to make this correction, as there are other sources of error of greater magnitude.

² The mho is the reciprocal ohm.

The resistance of a cell filled with $N/50$ potassium chloride at 25°C . was 550 ohms. The conductivity of $N/50$ KCl at this temperature is 0.002768. The cell was then washed out and filled with an $M/10$ solution of zinc sulphate at the above temperature. Its resistance was then 72.18 ohms. What are the molecular and equivalent conductivities of the zinc sulphate solution?

The cell constant is first obtained. This is equal to the conductivity of the KCl divided by the conductance measured. Conductance = $1/\text{resistance}$, and for the solution of KCl = $1/550$ reciprocal ohms, or mhos. Hence, the cell constant

$$k = 0.002768 / 1/550 = 550 \times 0.002768 \\ = 1.523.$$

The conductivity of the zinc sulphate solution is therefore

$$\frac{1.523}{72.18} = 0.02110.$$

The molecular conductivity is the conductivity multiplied by the volume in c.c. containing one gram-molecule, in this case 10,000 c.c. Hence, the molecular conductivity is

$$0.02110 \times 10,000 = 211.0.$$

The equivalent conductivity is the conductivity multiplied by the volume containing one equivalent of the electrolyte. The equivalent of zinc sulphate is one-half of the molecular weight. The volume containing this will be 5 litres, and so the equivalent conductivity is 105.5.

299. Variation of Conductivity with Dilution.—Although the actual conductivity of an electrolyte becomes smaller as the solution is progressively diluted, the molecular and equivalent conductivities increase with dilution until a maximum limiting value is reached. Curves for a few typical substances are shown in Fig. 191. The figures for potassium chloride are given in Table LXXVI. Note that the conductivity decreases, but the equivalent conductivity increases with increasing dilution.

300. Degree of Dissociation.—The limiting value approached by the equivalent conductivity as the solution is diluted is called the *equivalent conductivity at infinite dilution*. The amount of current passing clearly depends upon the number of ions present in the solution, for they are the sole carriers of the current, and also upon their mobility, or the ease with which they get through the liquid. The two factors, then, upon which the conductivity of a solution will depend are (a) the number of ions and (b) their mobility. Arrhenius assumed that the latter did not vary with dilution, and so the only reason for the increased equivalent conductivity must lie in the formation of more ions. At infinite dilution he supposed that the electrolyte was completely dissociated. Since the

TABLE LXXVI.—CONDUCTIVITY OF POTASSIUM CHLORIDE SOLUTION AT 18° C.

Concentration gm.-equiv. per litre.	Volume containing 1 gm.-equiv. V c.c.	Conductivity κ .	Equivalent Conductivity $\Lambda = \kappa V$.	Apparent degree of Dissociation. $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$
0	∞	—	(129.9)	(1.00)
0.0001	10,000,000	0.00001291	129.1	0.994
0.001	1,000,000	0.0001273	127.3	0.980
0.01	100,000	0.001224	122.4	0.943
0.1	10,000	0.0112	112.0	0.862
1.0	1,000	0.0983	98.3	0.757

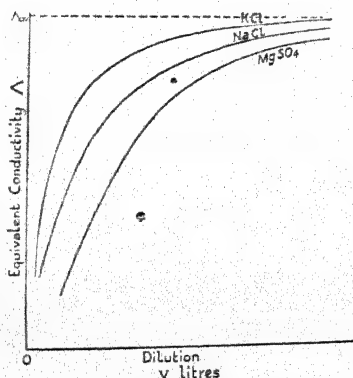


FIG. 191.—Showing the Form of the Conductivity-dilution Curve.

current flowing is proportional to the number of ions present, the amount of dissociation at any dilution will be given by

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty}$$

α is called the degree of dissociation of the electrolyte, and, of course, varies with the dilution. Λ_v is the equivalent conductivity at dilution v (i.e., one gram-equivalent dissolved in v c.c. of solution), and Λ_∞ is that at infinite dilution. This is an extremely important relationship and will be frequently used in what follows.

It must be borne in mind that although all electrolytes give a value for α , it is now believed that strong electrolytes are completely dissociated at all dilutions, and that α for them represents the effect of interionic forces on the mobility of the ions. It is therefore called the "apparent degree of dissociation" for strong electrolytes.

301. Effect of Dissociation on Osmotic Pressure and other Colligative Properties.—It has already been mentioned that the osmotic pressure laws do not apply to electrolytes, and that van't Hoff used the expression

$$PV = iRT$$

to take account of these anomalies (§ 291). It follows that i is equal to the ratio of calculated molecular weight to the observed value. It is found that the values of i are practically the same whether they are derived from osmotic pressure or freezing point observations. i varies with the dilution of the solution.

The very fact that there is such a factor as i which must be introduced

in the osmotic pressure equation to explain the observations means that the molecules may be broken down into smaller parts. The natural assumption to make, when the facts of electrolysis are known, is that these parts are the ions, and this is largely confirmed by the values of i obtained. Thus, for potassium chloride, the value is 1.88; for magnesium chloride it is 2.68, and for calcium nitrate it is 2.41, the dilution in all cases being 20 litres (i.e., 1 gm.-equivalent is dissolved in 20 litres). It will be noted that for a substance which splits into two ions (such as potassium chloride), the value of i approximates to 2, whilst for those which split into more than two ions it is greater than 2. The best proof of the connection between the phenomena of osmotic pressure and electrolysis is given by the fact that the degree of dissociation found from electrical conductivity agrees fairly well with that obtained from the osmotic pressure figures. If α is the degree of dissociation, then

$$i = (n - 1) \alpha + 1,$$

where n is the number of ions formed from one molecule of the electrolyte. The derivation of this equation is given in § 291. The figures in Table LXXVII enable a comparison to be made.

TABLE LXXVII.—DEGREE OF DISSOCIATION FROM FREEZING POINT AND CONDUCTIVITY OBSERVATIONS

Substance.	Dilution. Volume in Litres con- taining 1 gm.-equiv.	i .	α from Freezing Point.	α from Conductivity.
Potassium chloride $n = 2$	200	1.96	0.96	0.97
	20	1.88	0.88	0.90
Potassium nitrate $n = 2$	200	1.96	0.96	0.95
	20	1.85	0.85	0.87
Hydrochloric acid $n = 2$	200	1.99	0.99	0.98
	10	1.91	0.91	0.92
Nitric acid $n = 2$	200	1.97	0.97	0.98
	5	1.87	0.87	0.92
Sodium hydroxide $n = 2$	200	1.99	0.99	0.96
	20	1.83	0.83	0.91
Calcium nitrate $n = 3$	20	2.41	0.70	0.73
	10	2.41	0.70	0.68
Potassium ferrocyanide $n = 5$	40	3.32	0.58	0.54
	10	2.79	0.45	0.46

The fact that the values of α obtained from conductivity and freezing point observations do not agree exactly for strong electrolytes points to the conclusion that the degree of dissociation for these substances is only apparent. As has been pointed out already, α is not a degree of dissociation for strong electrolytes, but a measure of the interionic forces.

302. Conductivity of Strong Electrolytes.—In previous sections it was pointed out that the conductivity of a solution of electrolyte depends on the number and the mobility of the ions present. It was also stated that Arrhenius assumed that the mobility of an ion was constant with variation in concentration and that the variation of conductivity with concentration was accounted for by a variation in the degree of dissociation of the electrolyte present. While the Arrhenius theory is adequate for weak electrolytes it does not hold for the strong electrolytes. It can be shown by several methods that strong electrolytes are totally ionised at all concentrations. One most striking illustration of this is the X-ray diffraction pictures of solid electrolytes which show that these compounds are ionised even in the solid state. The effect of dissolving the salt is merely to weaken the interionic forces. This is due to the high dielectric constant of the solvent, in this case water. The force between electrical charges, e_1 and e_2 is given by the equation $\frac{e_1 e_2}{r^2 D}$ where r is the distance between the

charges, and D is the dielectric constant. In a vacuum D is 1 and in air the value is slightly greater than 1. The dielectric constant of water is 81. The effect of dissolving a salt in water is to reduce the attractive forces between the ions of opposite charge to about one-eightieth of their value in air, and so the ions are free to move independently in solution. The effect of the dielectric constant of the solvent in the dissociation of a salt is considered again later (§ 312). The modern theory of strong electrolytes assumes that the variation of conductivity with concentration is caused by a variation in mobility of ions with concentration. This theory was originally devised by Debye and Hückel. It takes account of the electrostatic forces between the ions. The main flaw in Arrhenius's theory is that these interionic forces are ignored.

There is a tendency for an ion in solution to be surrounded by ions of opposite charge. We can think of each ion as being associated with an ionic atmosphere of opposite charge. When a potential is applied across a solution the ions will move to the electrodes; the cations will move towards the cathode and the anions towards the anode. The motion of an ion towards an electrode is opposed by the ionic atmosphere in two ways. Firstly, as the ion moves its atmosphere will tend to build up in front of the ion and die away behind it. If this process of building up and dying away were instantaneous the atmosphere would always be symmetrically placed about the ion; in fact a finite time is required for the build up and die away—this is called the time of

relaxation. The result is that the atmosphere is asymmetrical about the ion during its motion; the centre of the atmosphere remains behind the ion with the result that the motion of the ion is retarded by the atmosphere. The effect is known as the relaxation effect. In addition the effect of an applied field produces a movement of an ionic atmosphere in a direction opposite to the movement of the ions. This motion of the atmosphere in the direction opposite to the ions produces another retarding effect on the motion of the ion; this effect is called the electrophoretic effect.

As the concentration of ions in a solution gets less the radius of the atmosphere about each ion will increase and both electrophoretic and relaxation effects will decrease. Hence the mobility of the ion will increase. The original calculations of Debye and Hückel were improved by Onsager. He deduced an equation of the form

$$\Lambda_c = \Lambda_\infty - (A \Lambda_\infty - B)\sqrt{2C}$$

where A and B are constants and c the concentration of ions in the solution. Plots of Λ_c against $\sqrt{2C}$ for various salts at low concentrations give straight lines, the slopes of which are those predicted by the Debye-Hückel-Onsager equation. At higher concentrations experimental and theoretical curves are not in such good agreement. This is due to two causes: firstly in the calculation a number of assumptions are made that only apply to dilute solutions; secondly at higher concentrations effects such as ion association may come into play. The theory does not allow for such effects.

While the variation of conductivity of strong electrolytes is due mainly to changes in ionic mobility the variation of conductivity for weaker electrolytes is mainly attributed to the variation in the degree of dissociation. However, the ionic atmosphere effects also operate for weaker electrolytes although, of course, they are much smaller than for strong electrolytes because the number of ions is much smaller. For a complete theory of weak electrolytes the Arrhenius theory must be modified by inclusion of these effects.

303. Conductivity and Viscosity.—Experiments have been carried out which indicate that there is an increase of resistance of the solution with increase in viscosity, the ions being hindered in their motion; but this effect is not simply bound up with the viscosity. It has been supposed that the conductivity is inversely proportional to the viscosity, but it is probable that the law is not so simple as this. If it were, there should be very little conductance through an electrolyte dispersed in a jelly, whereas the conductivity appears to suffer very little by this.

304. Effect of Temperature on Conductivity.—The conductivity of an electrolyte rises with temperature. The effect is probably due chiefly to alteration of the mobility of the ions, and not of their number. In

turn, this variation of mobility may be affected by change in viscosity of the solution.

305. The Independent Mobility of Ions.—Kohlrausch, from a study of the equivalent conductivity of various electrolytes at infinite dilution, found certain relationships. Thus, if we take the two salts potassium chloride and nitrate, and compare their equivalent conductivities at infinite dilution with those of the corresponding sodium salts, we have

	Potassium.	Sodium.
Chloride	130.10	108.99
Nitrate	126.50	105.33

The value $(\text{KCl} - \text{KNO}_3) = 3.60$, whilst $(\text{NaCl} - \text{NaNO}_3) = 3.66$. $(\text{KCl} - \text{NaCl}) = 21.11$, and $(\text{KNO}_3 - \text{NaNO}_3) = 21.17$. Thus, the difference of two anions is constant, as is also the difference of two cations. This led Kohlrausch to state that the equivalent conductivity at infinite dilution was made up of two parts, that due to the anion and that due to the cation. If we have a salt such as silver nitrate, its equivalent conductivity at infinite dilution will be the sum of two terms, one due to the silver, and the other to the nitrate ion. These terms were called the "mobilities". The law is known as the Law of Independent Mobilities.

It is obvious that once one mobility is known (this can be obtained by a transport number experiment, § 307), all the rest can be obtained from the experimental values of Λ_∞ for different salts.

The values of some ionic mobilities are given in the Table.

TABLE LXXVIII.—IONIC MOBILITIES

Ion.	Mobility.	Ion.	Mobility.	Ion.	Mobility.	Ion.	Mobility.
Li	33.4	Cs	68	$\text{C}_2\text{H}_3\text{O}_2$	35	$\frac{1}{2}\text{Cu}$	45.9
Na	43.4	H	313.9	OH	174	$\frac{1}{2}\text{Cd}$	46.4
F	46.6	NH_4	64.3	NO_3	61.8	$\frac{1}{2}\text{Sr}$	51.9
Ag	54.3	$\frac{1}{2}\text{Mn}$	28	ClO_4	64	$\frac{1}{2}\text{Ba}$	55.4
K	64.6	$\frac{1}{2}\text{Co}$	43	$\frac{1}{2}\text{Ni}$	44	$\frac{1}{2}\text{Pb}$	60.8
Cl	65.5	SCN	56.7	$\frac{1}{2}\text{Fe}^{..}$	45	$\frac{1}{2}\text{SO}_4$	68.5
Tl	65.9	IO_3	34.0	$\frac{1}{2}\text{Fe}^{...}$	61	$\frac{1}{2}\text{CrO}_4$	72
I	66.25	ClO_3	54.87	$\frac{1}{2}\text{Cr}^{...}$	45	$\frac{1}{2}\text{CO}_3$	60
Br	67.7	BrO_3	47.6	$\frac{1}{2}\text{Mg}$	45.9	$\frac{1}{2}\text{Fe(CN)}_6^{....}$	95
Rb	67.5	IO_4	48	$\frac{1}{2}\text{Zn}$	47.0	$\frac{1}{2}\text{Al}$	40

By means of these values it is possible to calculate the equivalent conductivity of any electrolyte at infinite dilution. Thus, the value of the equivalent conductivity of potassium sulphate $\frac{1}{2}\text{K}_2\text{SO}_4$ at infinite dilution = $64.6 + 68.5 = 133.1$.

The Table shows that the hydrogen and hydroxyl ions have much greater mobilities than any of the other ions. It must be remembered that these are not the absolute velocities of migration of the ions (§ 308).

The Law of Independent Mobilities is especially useful where the experimental determination of the conductivity at infinite dilution cannot be carried out with accuracy owing to the high value of the resistance. Thus, to find the conductivity of acetic acid at infinite dilution, we may determine that of hydrochloric acid, potassium acetate, and potassium chloride. In all these cases the experimental determination is possible, as the resistances are not too high. Then, if the Law of Independent Mobility of Ions is true,

$$\Lambda_{\infty} \text{KCl} = [\text{K}] + [\text{Cl}],$$

$$\Lambda_{\infty} \text{KAc} = [\text{K}] + [\text{Ac}],$$

$$\Lambda_{\infty} \text{HCl} = [\text{H}] + [\text{Cl}],$$

$$\therefore [\text{H}] + [\text{Ac}] = [\text{H}] + [\text{Cl}] + [\text{K}] + [\text{Ac}] - \{[\text{K}] + [\text{Cl}]\}.$$

$$\text{or, } \Lambda_{\infty} \text{HAc} = \Lambda_{\infty} \text{HCl} + \Lambda_{\infty} \text{KAc} - \Lambda_{\infty} \text{KCl},$$

where symbols in square brackets denote mobilities.

306. Transport Numbers.—The fact that in electrolysis the ions move with different speeds causes changes in concentration round the electrodes. The way in which this change is connected with the speed of the ions is best shown by means of a diagram. In Fig. 192 the black dots represent anions and the circles cations. In a molecule the two may be supposed to be in conjunction.

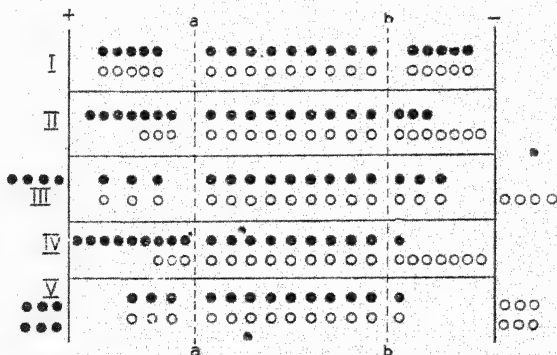


FIG. 192.—To illustrate Unequal Mobility of Ions.

We shall divide the solution into three compartments by means of imaginary partitions, *aa* and *bb*. The state of the solution before electrolysis may be represented by the line I. Here every anion is

associated with a cation. This does not mean that dissociation has not taken place, but since there is random motion, and there are exactly as many anions as cations, the probability is that an anion will find itself in the neighbourhood of a cation. Suppose that the ions move with the same speed; then whilst, say, two anions have crossed the partitions towards the anode, two cations will have crossed in the opposite direction towards the cathode. The state of the solution is shown in line II. Line III shows these ions liberated and also the fact that, though both anode and cathode compartments have become weaker, they have become so to the same extent.

Now suppose the anion moves twice as fast as the cation. Four anions will therefore pass across the partitions towards the anode, and only two cations will pass to the cathode. The state of the solution is now as in IV. After liberation of the ions at the electrodes, there are twice as many undischarged anions and cations in the anode compartment as there are in the cathode compartment. Thus, the fall of concentration at the anode divided by that at the cathode is equal to 1/2. Thus

$$\frac{\text{loss at anode}}{\text{loss at cathode}} = \frac{\text{speed of cation}}{\text{speed of anion}}$$

It is useful to remember that the loss at any compartment is proportional to the speed of the ion which is leaving it. The student should convince himself of the truth of this statement by trying other relative speeds, such as 5/3. The remarkable fact that although the amounts of substance liberated at each pole are equivalent, yet one ion moves faster than the other, is thus accounted for.

Suppose that a fraction of the current n is carried by the anion; then an amount $1 - n$ must be carried by the cation. Since the amounts of electricity carried are proportional to the speeds of the ions (§ 300), we have

$$\frac{\text{loss at anode}}{\text{loss at cathode}} = \frac{1 - n}{n},$$

or, the value n is given by

$$n = \frac{\text{fall in concentration round cathode}}{\text{total fall round anode and cathode}}$$

Hittorf, to whom the above reasoning is due, called n the transport number of the ion. If n is the transport number of the anion, then $1 - n$ must be that for the cation. If u is the velocity of the anion, and v that of the cation, then

$$\frac{n}{1 - n} = \frac{\text{loss at cathode}}{\text{loss at anode}} = \frac{u}{v}$$

307. Determination of Transport Numbers.—It was a condition of the above reasoning that the concentration in the middle compartment remained constant. Hence, in any experimental determination of transport numbers care must be taken that this is fulfilled. Hittorf used sodium chloride solution as electrolyte, a cadmium anode, and a platinum cathode. The action of the chlorine liberated at the anode produces cadmium chloride, and the cadmium ions move towards the cathode. Being much slower than the sodium ions, they never catch them up, and the cadmium chloride therefore remains as a separate layer. At the cathode all the chlorine ions have gone away, and are

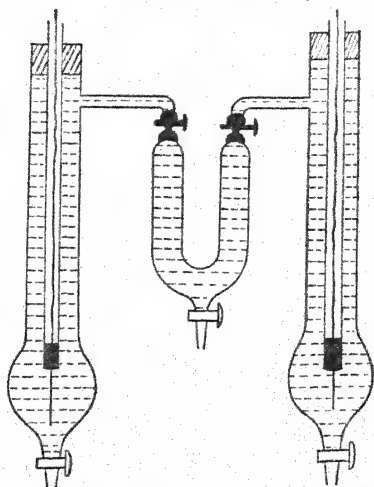


FIG. 193.—Transport Number Tube.

replaced by hydroxyl ions produced by the action of the sodium liberated there on the water. These ions are fairly fast, and therefore pass down into the solution, producing mixing. An apparatus is shown in Fig. 193. Here the three portions are tapped and can be run off for analysis without disturbing the rest.

The following are some results of the Hittorf experiment, and are given to show the method of calculation.

The original solution contained 0.01784 per cent. chlorine, the weights of chlorine in the three parts of the apparatus before and after electrolysis being

	Before.	After.
Anode part . . .	0.04048 gm.	0.04671 gm.
Central part . . .	0.03482 „	0.03483 „
Cathode part . . .	0.05913 „	0.05289 „

Note that the composition of the central part remained unchanged, within the limits of experimental error.

The weight of silver deposited in a silver voltameter connected in series with the transport number tube was equivalent to 0.01021 gm. chlorine.

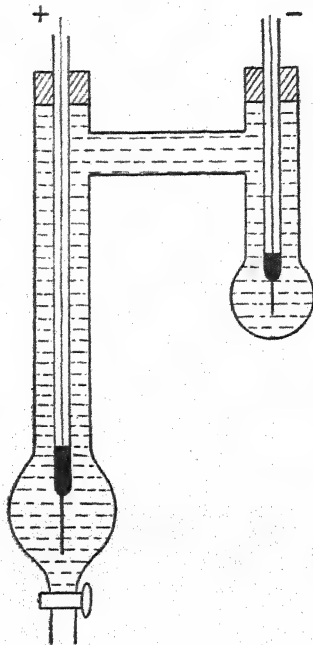


FIG. 194.—Transport Number Tube.

From the above data, the gain in the anode part was 0.00623 gm., whilst the loss in the cathode part was 0.00624 gm.

The transport number of Cl^- in the electrolyte is therefore

$$n = \frac{\text{loss round cathode}}{\text{total loss}} \\ = \frac{0.00624}{0.01021} = 0.611.$$

The transport number of the sodium ion is therefore 0.389.

The common form of transport number tube used in elementary work is shown in Fig. 194. Suppose it is to be used in the determination of the transport numbers of the silver and nitrate ions in silver nitrate solution. Suppose that both electrodes are of platinum, and that the solution of silver nitrate has deposited on the cathode, during the

electrolysis, 1.2591 gms. of metallic silver. A certain volume of the solution taken from the region of the anode now contains 12.5533 gms. of silver, whereas before it contained 13.1426 gms. The solution at the anode has therefore lost 0.5893 gm. of metal. The total loss is 1.2591 gms. of silver. Hence, the transport number of the cation

$$\begin{aligned} n &= \frac{\text{loss round anode}}{\text{total loss}}, \\ &= \frac{0.5893}{1.2591} = 0.457. \end{aligned}$$

The transport number of the anion is therefore $1 - 0.457 = 0.543$.

In some forms of the apparatus the anode is of silver. In this case a silver voltameter must be connected in the circuit, but the calculation is of similar form to the above.

TABLE LXXIX.—TRANSPORT NUMBERS OF ANIONS OF SALTS IN *M*/10 SOLUTION AT 18°C.

Salt.	Transport Number of Anion.	Salt.	Transport Number of Anion.
KCl . . .	0.508	AgNO ₃ . . .	0.528
KBr . . .		KOH . . .	0.735
NH ₄ Cl . . .		HCl . . .	0.172
KI . . .		$\frac{1}{2}$ BaCl ₂ . . .	0.585
NaCl . . .	0.617	$\frac{1}{2}$ CdI ₂ . . .	0.71
LiCl . . .	0.69	$\frac{1}{2}$ CuSO ₄ . . .	0.632
KNO ₃ . . .	0.497		

The arrangement of apparatus for carrying out a determination of the transport numbers of the silver and nitrate ions is shown in Fig. 195. Suppose the transport number tube is fitted with a silver anode, and a platinum cathode. *V* is a silver voltameter, made by placing two pieces of platinum foil, mounted on platinum wires, in silver nitrate solution. A solution containing 17 gms. of silver nitrate in 1,000 gms. of water is made up, and 100 gms. of this solution are weighed into the voltameter. The transport apparatus is filled with the silver nitrate solution. A small current is required for this experiment. A 50-volt battery is convenient; if not available, a suitable resistance may be placed in the mains (which must be direct current, not alternating). The current is passed for about five hours. While the electrolysis is proceeding, two 50-gm. portions of the silver nitrate solution are weighed out and titrated against standard potassium thiocyanate (*N*/10). When the experiment is finished, about as much liquid as would fill the anode

limb is run off from the transport apparatus into a weighed flask, and weighed. It is then titrated with $N/10$ potassium thiocyanate. The silver solution from the voltameter is also titrated. From these results the required transport numbers can be obtained.

To show the method of calculation, let the 50 gms. of silver nitrate solution started with require x c.c. of $N/10$ potassium thiocyanate. The titre of the solution in the voltameter at first would therefore be $2x$.

Let its titre at the end of the experiment be y c.c. Then the amount of current passed is proportional to $2x - y$.

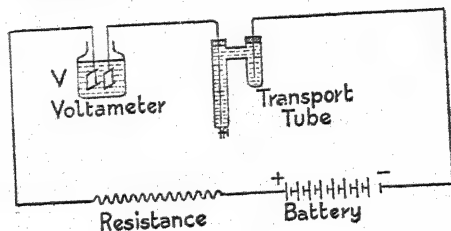


Fig. 195.—Apparatus for determining Transport Numbers.

The anode solution weighs w gms. and requires z c.c. of thiocyanate. But, an amount of silver proportional to $2x - y$ c.c. of thiocyanate has been dissolved from the anode by the passage of the current. Hence, the amount of the original silver nitrate left is proportional to $z - (2x - y)$.

The silver nitrate originally present in w gms. of solution corresponds to $w \times 50$ c.c. potassium thiocyanate. Hence, loss of silver from the anode is proportional to $(wx/50) - z + 2x - y$ c.c. potassium thiocyanate. Hence, the transport number for the cation (silver)

$$= \frac{\text{loss at anode}}{\text{total loss}},$$

$$= \frac{(wx/50) - z + 2x - y}{2x - y}.$$

308. Absolute Velocity of Ions.—The ionic mobilities of Kohlrausch are not the absolute velocities of the ions. In determining the absolute velocity of ions it is clear that the speed will depend on the potential gradient in the solution. It is therefore necessary to specify this, and the absolute velocity is measured in cm. per sec. for a potential gradient of 1 volt per cm.

Consider the solution in a centimetre cube, the electrodes being at the shaded faces. Let there be a potential of 1 volt between them. The current flowing through the cell will then be numerically equal to the specific conductivity, κ (by definition), and will be in amperes. Let the concentration be c , and let it be so small that the solution may be

assumed to be completely ionised. The amount of electricity passing through the cube in one second will be

$$\kappa = cA\infty = c(u + v),$$

where u is the ionic mobility of the anion, and v is that of the cation (§ 305).

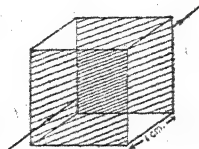


FIG. 196.

Let U and V be the absolute velocities of the anions and the cations respectively. All the anions within a distance U cm. of the anode will have moved up to it in one second, and all cations within a distance V cm. from the cathode will have moved up to it in one second. These correspond to Uc and Vc gm.-equivalents respectively, since 1 c.c.

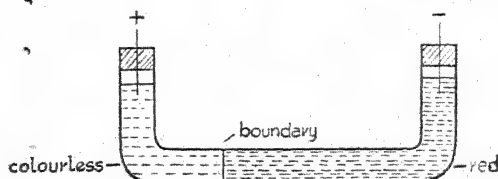


FIG. 197.—Lodge's Tube.

contains c gm.-equivalents. They will involve the transfer of 96,500 $(U + V)c$ coulombs (from Faraday's Second Law, § 295).

Hence, $96,500(U + V)c = c(u + v).$

Since $A\infty = u + v,$

$$U = \frac{u}{96,500}, \text{ and } V = \frac{v}{96,500}.$$

The absolute velocities of the ions are therefore obtained by dividing the ionic mobilities by 96,500. The ionic mobility of the hydrogen ion is 313.9; hence, its absolute velocity is $313.9/96,500$

= 0.00325 cm. per sec. for a potential gradient of 1 volt per cm.

The absolute velocities of the ions are much smaller than one would suppose. The fastest of them, the hydrogen ion, moves only with a velocity of 0.00325 cm. per sec., under a potential gradient of 1 volt.

The actual velocity of the ions can be observed by Lodge's moving boundary method. A tube of the form shown in Fig. 197 is filled with a

jelly of agar-agar, phenolphthalein being added, and the whole being coloured red by the addition of a trace of alkali during the preparation of the jelly. When the jelly has set, sodium sulphate solution is added to one side, and dilute sulphuric acid to the other. On passing the current, hydrogen ions pass along the solution, and their rate of motion can be followed by noting the progressive loss of colour of the jelly, owing to the neutralisation of the base by the hydrogen ions. The value for the mobility of the hydrogen ion was found to be 0.0025 cm./sec.

The method was improved by Whetham, who used two solutions with a common ion of the same concentration and almost the same conductance. One of these was coloured and the other not. The substances chosen were potassium dichromate and potassium carbonate.

The coloured ion moved, and its rate of motion could be followed by noting the position of the boundary. The current was measured, and from the results the absolute mobilities were obtained, the results agreeing with those of Kohlrausch.

The method may be applied to the determination of transport numbers (see Fig. 198). A solution of a salt to be investigated, BA, is placed in a layer between layers of solutions of two other salts each of which has an ion in common with BA. For example BA may be potassium chloride, B'A lithium chloride and BA' potassium acetate. The solutions are arranged in order of decreasing density upwards. The original boundaries are *ab*. Even if the solutions are colourless the boundaries may be observed because of differences between the refractive indices of the solutions. In order that the boundaries should remain sharp throughout the experiment B' and A' must have smaller velocities than B and A. When the current is passed the boundaries move to *b'* and *a'*. The distance *aa'* and *bb'* are proportional to speeds of the ions A and B.

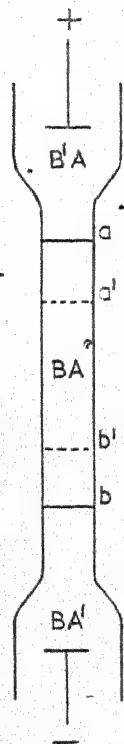


Fig. 198.—The Moving Boundary Method of determining Transport Numbers.

$$\text{The ratio } \frac{aa'}{aa' + bb'} = \frac{U}{U + V} = \text{transport number of cation while}$$

$$\frac{bb'}{aa' + bb'} = \frac{V}{U + V} = \text{transport number of anion.}$$

The study of transport numbers has indicated the existence of

hydration of the ions. If the transport numbers of the alkali metal ions are determined in $N/20$ solutions of the chlorides at 18°C ., the values given in Table LXXX are obtained (Glasstone).¹

It would be expected that the lightest ion would have the greatest mobility, but this is not the case. As far back as 1894 Bredig suggested that this might be due to hydration of the ions. If the ions were attached to water molecules, their size would be considerably increased. If this is so, the lithium ion must be heavily hydrated, and that of caesium very little. This is confirmed when the salts of these metals are considered, for in the crystalline state the salts are completely ionised.

TABLE LXXX

Metal.	Transport Number.	Atomic Volume.
Li	0.320	11.8
Na	0.386	23.7
K	0.496	45.3
Rb	0.485	56.0
Cs	0.492	70.7

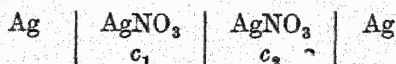
Thus, lithium salts are mostly hydrated, those of sodium frequently hydrated, whilst the number of hydrated salts met with decreases as the series is ascended. This view also follows from the electronic theory of valency (§ 79).

If an indifferent substance such as sugar is added to an electrolyte, the changes of concentration of this substance at the electrodes will depend on the transport numbers of the ions, and also upon the amounts of water which each ion carries. If a and b are the number of water molecules attached to each anion and cation respectively, then

$$na - (1 - n)b = x$$

is the amount of water molecules transported to the electrode per Faraday, n being the transport number of the anion. Experiments carried out in this way show that nearly all ions are hydrated. Reference to this will again be made in § 378. Evidence for hydration of ions also comes from freezing point observations. In strong solutions, the ions remove a certain amount of water from the solvent, and thus the solution appears to be stronger. In this way Jones was able to find the degree of hydration of various ions.

309.—Determination of Transport Numbers from Electromotive Force Measurements.—The e.m.f. of a concentration cell of the type



¹ S. Glasstone, "The Electrochemistry of Solutions" (Methuen).

where c_1 and c_2 are concentrations, involves the transport number of the anion. The determination can therefore be used to find transport numbers. The method is described in § 340.

310. Solubility of Sparingly Soluble Salts.—Conductivity measurements may be used to determine the solubility of sparingly soluble salts. If the solubility is s (gram equivalents per litre), and s is so small that we can consider the solution as being infinitely dilute then $\Delta_\infty = \frac{1,000\kappa}{s}$ where κ is the specific conductance. Δ_∞ can be calculated for a particular salt from the sum of its ionic mobilities, and κ can be measured, so s can be determined. For example, κ for silver chloride solution is $3.41 \times 10^{-6} \text{ ohm}^{-1} \text{ cms.}^{-1}$ at 25°C . As this is a very small conductance, allowance must be made for the conductance of water which is 1.6×10^{-6} so κ for silver chloride alone is 1.81×10^{-6} . Δ_∞ for silver chloride is $138.3 \text{ ohm}^{-1} \text{ cms.}^2$, and putting in these values gives $s = \frac{1,000 \times 1.81 \times 10^{-6}}{138.3} = 1.31 \times 10^{-5} \text{ gram. equivalents per litre at } 25^\circ \text{C}$.

311. Non-aqueous Solutions.—The study of solutions in solvents other than water has provided a considerable amount of information on the nature of electrolysis. The ions are all solvated to a certain extent in water, whereas in non-aqueous solvents this might not be the case.

It is not an easy matter to study non-aqueous solutions, as the presence of even a trace of water may seriously alter the results. The chief work has been done by Walden,¹ who employed in many of his experiments the compound tetraethylammonium iodide $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$, dissolved in various solvents. He discovered that the equivalent conductivity at infinite dilution of a salt is inversely proportional to the square root of its molecular weight and to the viscosity of the solvent.

Amongst the solvents used, those containing hydroxyl groups, such as methyl and ethyl alcohols, behave in a similar manner to water. The mobility of ions in various solvents has been found; the following are some of the results:—

	Water.	Methyl Alcohol	Ethyl Alcohol.	Acetone.	Nitromethane.
H^+	351	142	59.5	88	63
NH_4^+	74	58	19	98	64
K^+	74	54	22	82	60
Ag^+	63	50	17.5	90	53

¹ A great deal of the more modern work has been done by Hartley and his co-workers at Oxford.

It is seen that the hydrogen ion has a greater mobility in the hydroxylic solvents (with the exception of ethyl alcohol) than in the others. This may be due to the hydrogen ion being carried from a $[\text{H}_3\text{O}]^+$ ion to a water molecule, much as in the Grotthus chain explanation (§ 294), so that the calculated velocity is not that of the hydrogen ion itself, but the total effect of a number of hydrogen ions.¹ Goldschmidt has shown that the addition of a trace of water to an ethyl alcoholic solution of hydrogen chloride reduces the equivalent conductivity considerably, so that the hydration of the hydrogen ion which results must prevent it from taking part in this chain method of transference.

312. Effect of Dielectric Constant on Ionisation.—Walden showed that a dissolved salt gives a definite value for the ratio $\frac{\Lambda}{\Lambda_\infty}$ at a dilution which is inversely proportional to the cube of the dielectric constant of the solvent. Thus, if we choose $\frac{\Lambda}{\Lambda_\infty} = 0.5$, we shall find the dilution required to give this is inversely proportional to the cube of the dielectric constant. Some data are given in Table LXXXI. The ratio $\frac{\Lambda}{\Lambda_\infty}$ is 0.5. This relationship is only approximately true, and reaches this degree of accuracy only for strong electrolytes.

TABLE LXXXI.—ELECTROLYTIC DISSOCIATION AND DIELECTRIC CONSTANT (25° C.)

	Dielectric Const., D .	Dilution, v .	$D(v) \frac{1}{2}$ (nearest integer).
Silver nitrate in water	81	0.7	72
Sodium chloride in formic acid	62	2.1	79
Tetraethylammonium iodide in furfural	42	5.0	72
Potassium iodide in acetonitrile	36.4	11.0	81
Lithium nitrate in methyl alcohol	35.4	9.0	74
Lithium chloride in ethyl alcohol	26.8	35	88
Potassium iodide in acetone	21.2	60	83

It is found that only in liquids of fairly high dielectric constant can ionisation take place. The dielectric constant of a substance is dependent upon its dipole moment, *i.e.*, upon the degree of asymmetry of the arrangement of charges in the molecule (§ 402). It is not surprising

¹ Hückel, *Z. Electrochem.*, 1928, 34, 546. An account of the work done on this subject is to be found in the various volumes of *Annual Reports*, published by the Chemical Society, and particularly in the volume for 1930.

therefore to find that those liquids with high dielectric constants, *i.e.*, very unsymmetrical fields, can bring about ionisation.

The actual mechanism of ionisation in solution, where the solid salt is not completely ionised before dissolution, is not understood. Some hold the view that compound formation with the solvent is a necessary preliminary to further breakdown into ions.

The behaviour of salts in non-aqueous solvents is usually considerably different from that in water. Ionisation in any solvent is governed largely by Fajans' rule (§ 79). This states that ionisation will be promoted by the presence of a small anion and a large cation.

313. Degree of Dissociation in Non-aqueous Solvents.—Walden has found that the degree of dissociation of a dissolved salt is approximately constant for saturated solutions of substances in any solvent provided that water is rigidly excluded. The ratio of $\frac{\Lambda_v}{\Lambda_\infty}$ is given in

Table LXXXII for saturated solutions of tetraethylammonium iodide in various solvents. The constancy is remarkable.

By an examination of the equivalent conductivities of the thiocyanates and perchlorates of lithium, sodium, potassium and ammonium, in nitromethane at various dilutions, Wright, Murray-Rust and Hartley found that the empirical relationship

$$\Lambda_v = \Lambda_\infty - xc^3$$

was true. In this equation c is the concentration and x a constant. Salts of the tetraethylammonium radical, however, behave according to the equation

$$\Lambda_v = \Lambda_\infty - x\sqrt{c}.$$

TABLE LXXXII.—DISSOCIATION OF NEt_4I IN SATURATED SOLUTIONS AT 25° C.

Solvent.	Λ_v .	Λ_∞ .	$\frac{\Lambda_v}{\Lambda_\infty}$.
Methyl alcohol	47.85	124	0.40
Furfural	26.83	50	0.52
Acetonitrile	96.4	200	0.48
Acetone	112.4	225	0.50
Ethyl nitrite	68.67	140	0.49

314. Evidence in Favour of the Dissociation Theory.—(1) The reactions of salts in inorganic chemistry show that salts are made up of

two parts. Thus, all chlorides give the same reactions, whereas there are also reactions common, for example, to all potassium salts.

(2) Various physical properties of solutions of electrolytes are additive. Thus, surface tension, and density, may be regarded as the sum of three separate factors, one characteristic of the solvent, another of the cation, and the other of the anion.

(3) The heat of neutralisation of a strong acid by a strong base is a constant (§ 325).

(4) The colours of solutions at high dilution should be made up of that of the solvent and that due to the two ions. If the solvent is colourless, and one ion is colourless and the other coloured, the substances falling into this class should all possess the same colour. Thus permanganates have been shown all to possess the same absorption spectrum.

(5) The theory explains in a simple manner the anomalies in osmotic pressure, depression of the freezing point, and elevation of the boiling point shown by electrolytes (§ 301).

(6) X-ray analysis indicates that ions are present in some solids (§ 134).

(7) Ostwald's Dilution Law is obeyed fairly closely by weak electrolytes (§ 318).

(8) The theory explains precipitation, through the theory of the solubility product (§ 335).

(9) Dissociation is shown in certain experiments on the distribution coefficient (§ 321).

315. The Theory of Metallic Conduction.—The chief difference between metallic and electrolytic conduction lies in the fact that there is no decomposition or polarisation in the former. The current passes through the conductor without bringing about any chemical change. Further, the temperature variation of resistance is different in the two cases. In the case of a metal there is a minimum resistance at some definite temperature, whilst for electrolytes the resistance decreases continuously with increase of temperature.

The generally accepted theory is that the flow of the current in a metal is merely the flow of electrons, the positive ions being stationary. Various experiments have led to this conclusion, but they cannot be studied here. Drude, assuming that the electrons in a metallic conductor could be regarded as if they were gas molecules on the kinetic theory, obtained an expression for the conductivity of a metal,

$$\kappa = \frac{e^2 N l}{2 m v}$$

where e is the charge on the electron, N the number of molecules per unit volume, l the mean free path of the electron, m the mass of the electron and v its velocity. Assuming equipartition of energy, as in the

kinetic theory of gases (§ 123), we can replace $\frac{1}{2}mv^2$ by $\frac{3}{2}kT$, where k is

Boltzmann's constant, and T the absolute temperature. Thus

$$\kappa = e^2 N l v / 6 k T.$$

The thermal conductivity of a metal is also intimately related to the electrical conductivity, a fact which is shown qualitatively by the order of these two properties in a series of metals being approximately the same. A good electrical conductor is also a good heat conductor. Drude calculated that the thermal conductivity was given by

$$\theta = \frac{1}{2} N k l v.$$

Dividing thermal by electrical conductivity, we have

$$\frac{\theta}{\kappa} = \frac{3 k^2 T}{e^2} = T \times \text{const.},$$

which is known as the law of Wiedemann and Franz.

Some crystals, which consist of ions regularly spaced in a lattice (*e.g.*, sodium chloride), show this electronic type of conduction to a very small extent. When a point electrode is inserted at the surface of a crystal of sodium chloride, and a high potential is applied between it and an electrode elsewhere in the crystal, a small current flows, and a coloration of the crystal occurs in the neighbourhood of the point electrode. The colour varies with the temperature and nature of the crystal. Now it is known that the opacity of the metals is due to the fact that electrons are free in the space lattice of the crystal. The metal crystal lattice probably consists of a number of positive ions in the regular lattice, with a cloud of free electrons associated with the lattice, but not fixed. These are sometimes called "electron gas". They are the electrons which move through the metal when an external e.m.f. is applied. When, therefore, a coloration is observed in the neighbourhood of the electrode in the salt crystal, it is inferred that in this region there is electron gas. There are, however, some differences between this conduction by a salt and metallic conduction, for there is also electrolytic conduction in a solid salt.

316. Conductivity of Alloys.—If there is no chemical combination between the constituents of an alloy, and if there is no formation of solid solutions, the conductivity of an alloy is the sum of the conductivities of the constituents, according to their proportions. This is

known as the mixture rule. When solid solutions are formed, the resistance is considerably greater than that predicted by the mixture rule.

A study of the conductivity of alloys is useful in determining their nature. If the graph drawn between electrical conductivity and composition is a straight line it may be inferred that the components are not miscible. If a solid solution is formed, the conductivity-composition curve shows a flat minimum and falls rapidly at both ends from the values for the pure components (Fig. 199). There may be combinations of these two types, one part of the curve being linear, whilst the other shows a minimum. This shows that there is a limited concentration range where there is miscibility. The nature of the curve will also show whether chemical compounds are formed. If there is a sharp point on a curve, it indicates the existence of a chemical compound, but the reverse is not always true.

317. Effect of Temperature on Conductivity of Metals.—The general formula connecting the resistance (R) of a pure metal with temperature is

$$R = a + bT + cT^2,$$

where a , b , and c are constants, and T is the absolute temperature. The value of c is very small, so for small temperature ranges the third term may be neglected.

This expression has been made use of for determining temperatures by the platinum resistance thermometer, an excellent method of measuring both high and low temperatures.

The above expression only holds for ordinary temperatures. When the temperature is reduced so much that it is in the neighbourhood of the absolute zero, some metals are found to become super-conducting. Their resistance falls practically to zero, and a current once started in a closed ring of metal will go on flowing for a long while. The investigation (which is still proceeding) of this state has been done largely at Leyden. Certain metals have been found not to become super-conducting, but the resistance falls to a minimum and then rises again. Examples of this class are copper and platinum.

The existence of the super-conducting state shows that, at very low temperatures, the motion of the "electron-gas" (§ 315) through the metal is not hindered. There can be no interaction between the electrons and the positive ions. As the temperature increases, the phenomenon of resistance comes into play. This must be due to a friction-like, or viscosity, force exerted on the electrons, presumably by the positive ions.

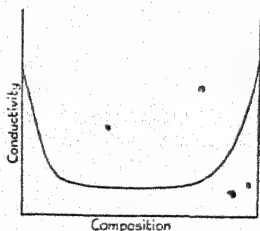


FIG. 199.—Conductivity Curve for Alloy forming Solid Solution.

SUGGESTIONS FOR FURTHER READING

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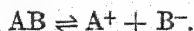
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CHAPTER XV

IONIC EQUILIBRIA

318. The Ostwald Dilution Law.—In a solution of a binary electrolyte there will be an equilibrium between the ions and the undissociated molecule, if the Arrhenius hypothesis is correct.¹ Thus, we have



It is therefore to be expected that the Law of Mass Action can be applied to this equilibrium just as it can to ordinary homogeneous equilibria. This application was first carried out by Ostwald (1888), and the result is known as *Ostwald's Dilution Law*.

Suppose that originally one gram-molecule of the binary electrolyte AB is dissolved in v litres of water, and that its degree of dissociation is α . Then



The quantities present at equilibrium are $\frac{1-\alpha}{v}$ of AB, $\frac{\alpha}{v}$ of A^+ , and $\frac{\alpha}{v}$ of B^- .

Applying the Law of Mass Action,

$$\frac{\left(\frac{\alpha}{v}\right)^2}{\frac{1-\alpha}{v}} = K,$$

$$\frac{\alpha^2}{v(1-\alpha)} = K \quad (1)$$

This is known as the Dilution Law.

If α is small compared with unity, it can be neglected in the denominator of the left-hand side of equation (1). In this case,

$$\frac{\alpha^2}{v} = K$$

$$\alpha = \sqrt{Kv}.$$

K is called the "*dissociation constant*"² of the substance. It is seen that,

¹ This excludes strong electrolytes which, as will be shown later, do not obey the Ostwald Dilution Law.

² K is also sometimes called the "*affinity constant*".

in the case of a weak electrolyte (i.e., α is small), the degree of dissociation is at a given concentration proportional to the square root of the dissociation constant.

The Law has been applied mainly to acids and bases. It is clear that the value of K will be a good measure of the strength of an acid, which is supposed to depend on the concentration of hydrogen ions in its solution (§ 326), for, as shown above, the degree of dissociation at a given concentration is proportional to the square root of K . A strong acid will be one with a large value for K in solutions of moderate concentration.

It is well to notice that the assumptions that are made in the derivation of this Law are that the Law of Mass Action applies to charged ions, and, even more fundamentally, that the Arrhenius hypothesis of electrolytic dissociation is true.

The Ostwald Dilution Law can be obtained in another form by substituting the value of $\alpha = \frac{\Delta_v}{\Delta_\infty}$ in the equation (1) above. This gives

$$K = \frac{\Delta_v^2}{v\Delta_\infty(\Delta_\infty - \Delta_v)}$$

The above formula would apply, of course, to a monobasic acid, such as acetic acid. Dibasic acids, however, ionise in two stages, and therefore possess two dissociation constants:—



The two dissociation constants are:—

$$K_1 = \frac{[\text{H}^+][\text{HA}^-]}{[\text{H}_2\text{A}]}$$

and

$$K_2 = \frac{[\text{H}^+][\text{A}^{--}]}{[\text{HA}^-]}$$

As a rule, for dilutions up to about 2,000 litres, the second stage is negligible. Thus, with hydrogen sulphide,

$$\frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 10^{-7},$$

and

$$\frac{[\text{H}^+][\text{S}^{--}]}{[\text{HS}^-]} = 10^{-15}.$$

319. Experimental Verification of the Dilution Law.—To test the law experimentally it is necessary to determine the degree of dissociation of a binary electrolyte at various dilutions, and then substitute the values of v and α in the Ostwald equation, and see if a constant is obtained:

The degree of dissociation is best determined by conductivity

observations. α is connected with the equivalent conductivity and that at infinite dilution by the equation

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty},$$

where Λ_v is the conductivity at dilution v , and Λ_∞ is that at infinite dilution (§ 300).

For the sake of example, suppose it is necessary to see whether Ostwald's Dilution Law holds for a weak acid such as propionic acid. The conductivity is determined at various dilutions by the ordinary method (§ 298). It is now necessary to find the equivalent conductivity at infinite dilution. As propionic acid is weak, it does not conduct well, with the result that the resistance of a very dilute solution is too great to be measured with accuracy. It is therefore necessary to apply Kohlrausch's method, which regards the equivalent conductivity at infinite dilution as made up of two parts, one due to the anion and the other due to the cation (§ 305). It is possible to determine the equivalent conductivity at infinite dilution of potassium propionate, potassium chloride and hydrochloric acid. If the quantities in square brackets represent the portion of the equivalent conductivity at infinite dilution due to the ions stated therein, we have

$$[\text{H}] + [\text{Pr}] = [\text{K}] + [\text{Pr}] + [\text{H}] + [\text{Cl}] - [\text{K}] - [\text{Cl}].$$

The conductivity of propionic acid at infinite dilution is thus determined. All that is now necessary is to substitute the values in the expression

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty}$$

when α is found. Now, using the value of α found at different dilutions,

TABLE LXXXIII.—IONISATION OF ACETIC ACID IN AQUEOUS SOLUTION
AT 25° C.

$$\Lambda_\infty = 387.9.$$

v .	Λ_v .	α .	$K = \frac{\alpha^2}{v(1-\alpha)}$.
0.334	0.6136	0.001595	7.7×10^{-6}
0.672	1.123	0.002896	12.5×10^{-6}
0.989	1.443	0.003636	14.0×10^{-6}
1.977	2.211	0.005701	16.5×10^{-6}
5.374	3.804	0.009806	18.1×10^{-6}
10.753	5.361	0.01382	18.0×10^{-6}
24.875	8.388	0.02163	19.2×10^{-6}
63.26	13.03	0.03359	18.5×10^{-6}

the equation of Ostwald can be tested. Table LXXXIII shows some values for acetic acid, and gives an indication of the validity of the Law for this substance.

It is clear that the Law is obeyed by acetic acid only in dilute solution (v large).

320. Validity of the Dilution Law.—Weak electrolytes obey Ostwald's Dilution Law fairly well, but in the case of strong electrolytes the Law fails completely. This "anomaly" of strong electrolytes has given rise to much interesting speculation on the nature of such solutions. The Table below, based on the work of Kohlrausch and Maltby, gives some figures for the ionisation of potassium chloride, which is a strong electrolyte.

TABLE LXXXIV.—APPARENT DEGREE OF IONISATION OF POTASSIUM CHLORIDE AT 18° C.

$$\Lambda_{\infty} = 129.91.$$

v .	Λ_v .	$\frac{\Lambda_v}{\Lambda_{\infty}} = \alpha$.	K .
1	98.27	0.7565	2.350
2	102.41	0.7883	1.434
5	107.96	0.8310	0.8154
20	115.75	0.8910	0.3642
50	119.96	0.9234	0.2221
200	124.41	0.9577	0.1084
1,000	127.34	0.9802	0.0485
10,000	129.07	0.9936	0.0154

It will be noted that the values of K are by no means constant.

In order to remove this anomaly, many empirical formulæ have been suggested as dilution laws, very few of them having any theoretical basis. Thus, Walker put forward the equation

$$\frac{\alpha^2}{(1 - \alpha)v} = k \frac{1 - \alpha}{\alpha},$$

or

$$k = \frac{\alpha^2}{(1 - \alpha)^2 v}.$$

Van't Hoff put forward the equation

$$\frac{\alpha^3}{(1 - \alpha)v^2} = k.$$

Possibly the best of all the formulæ for expressing the conductivity of strong electrolytes is

$$\Delta_{\infty} - \Delta_v = kC^{\frac{1}{2}},$$

where C is the concentration, or the reciprocal of v . This equation is ascribed to Kohlrausch, though it appears to have been put forward originally by Bousfield in 1913.

If this equation be true, it is obvious that if $\Delta_{\infty} - \Delta_v$ is plotted against $C^{0.5}$, a straight line should result, passing through the origin. The slope of the line should be k . Or, if Δ_v is plotted against $C^{0.5}$, again

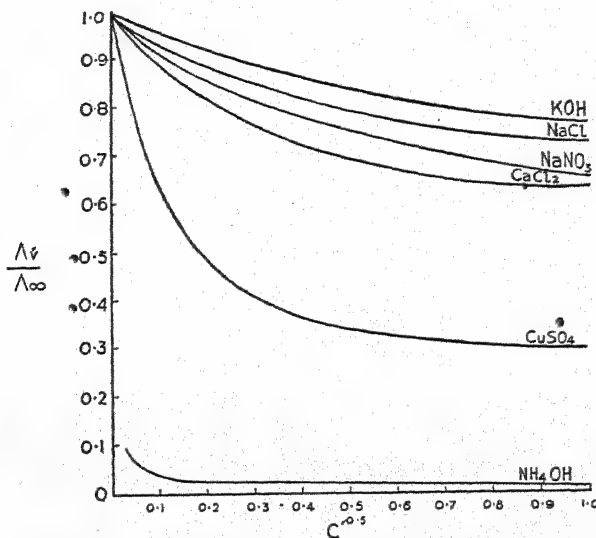


FIG. 200.—Curve between Δ_v/Δ_{∞} and $C^{0.5}$.

a straight line graph should be obtained, but it will not now pass through the origin, but will cut the axis at Δ_{∞} . It is usual to plot $\frac{\Delta_v}{\Delta_{\infty}}$ against the square root of the concentration, and in Fig. 200 are given some curves for various substances. The data upon which the curves are based are given in Table LXXXV. It is seen that the equation is only approximately true, holding best for the more dilute solutions. It is, however, very important as a limiting law for very dilute solutions. It may be noted here that the equation is of the form derived by Debye and Hückel on the basis of the theory of electrostatic interaction (§ 302).

321. The Anomaly of Strong Electrolytes.—As stated previously, the Ostwald Dilution Law does not hold for strong electrolytes; and even weak electrolytes show deviations from it as the concentration of solutions rise. It is also found that the expressions for the electro-

TABLE LXXXV.—CONDUCTANCE RATIOS

Substance.	$\frac{\Delta v}{\Delta \infty}$ for c (gm.-mols. per litre).			
$\sqrt{\frac{c}{c}}$	$\frac{0.01}{0.3162}$	$\frac{0.1}{1}$	$\frac{1}{3.162}$	$\frac{1}{1}$
Sodium chloride . . .	0.977	0.936	0.852	0.741
Sodium nitrate . . .	0.977	0.932	0.832	0.660
Calcium chloride . . .	0.954	0.882	0.764	0.662
Copper sulphate . . .	0.862	0.629	0.396	0.309
Potassium hydroxide . .	0.99	0.96	0.90	0.77
Ammonium hydroxide . .	0.118	0.042	0.014	0.0037

motive force of concentration cells expressed in terms of concentration fail to agree with experimental values as the concentrations rise.

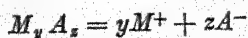
The Ostwald Dilution Law was calculated on the basis of two assumptions, viz.: (1) that the Law of Mass Action holds for charged ions; and (2) that the Arrhenius hypothesis, that electrolytes are partially dissociated into their ions in aqueous solution, is true, the ratio $\frac{\Delta v}{\Delta \infty}$ representing the extent of this dissociation. Since strong electrolytes do not obey the Law, it is clear that one, or both, of these assumptions is not true.

As far as the first assumption is concerned, the theoretical values may be brought into conformity with the experimental by writing the Law of Mass Action in the form:

$$K = \frac{a_+ a_-}{a_2}$$

where a_+ , a_- and a_2 are called the activities of the cation, anion, and undissociated electrolyte respectively. The activity is related to concentration c by the equation $a = fc$ where f is called the activity coefficient. The activity coefficient varies with concentration but as the concentration becomes small f tends to 1. In other words the Law of Mass Action can be applied to dilute solutions using concentrations only.

The activity coefficient of an individual ion cannot be measured experimentally. What is measured is the mean ionic activity coefficient. For the ionic dissociation



the mean ionic activity coefficient is defined by the relationship

$$f_{\pm} = (f_+^y f_-^z)^{\frac{1}{(y+z)}}$$

The relationships deduced for ideal systems may be applied to real systems if c is replaced by a ; thus, the e.m.f. of a concentration cell (see § 338) becomes

$$E = \frac{RT}{nF} \log e \frac{a_2}{a_1}.$$

Originally the activity coefficient was regarded as an empirical quantity. However, Debye and Hückel devised a method of calculating activity coefficients based on the conception of the complete dissociation of strong electrolytes. The expression $RT \log_e f$ expresses the difference between the free energy of formation of an ideal solution and that of an electrolyte. Debye and Hückel equated this expression with the free energy per mole of electrolyte due to the electrical interaction of ions. This interaction is not allowed for in simple solution theory. In calculating the interaction energy Debye and Hückel made use of the idea of each ion being surrounded by an atmosphere of oppositely charged ions. This conception has been discussed in the previous chapter (§ 302).

The activity coefficients calculated by Debye and Hückel for solutions of low concentration agreed with those experimentally measured. As with the conductivity theory, experiment and theory show deviations at higher concentrations. The deviations in the theoretically deduced activities are caused by the same factors that invalidated theoretically deduced conductivities. Although the Debye-Hückel theory was primarily advanced to solve the problems presented by strong electrolytes, its conclusions may be applied to weak electrolytes provided allowance is made for their incomplete dissociation. For example the Ostwald Dilution Law, when activity coefficients are

included, becomes: $K = \frac{a^2 c f_M f_A}{(1-a) f_{MA}}$, and by using the values of activity

coefficients calculated by the Debye and Hückel method K may be calculated. It is found that the K so calculated remains constant over a very large range of concentrations.

Although the theory of strong electrolytes that has been used above is that of complete dissociation, it is very probable that even in the strongest electrolytes there is not 100 per cent. dissociation. It would be better to say that there is "almost complete dissociation". If it were possible to draw a sharp dividing line between strong and weak electrolytes, it might be argued that the one class was quite different from the other, and that the strong electrolytes were completely dissociated, and the weak electrolytes only partially so. This is not possible, however, for there is a gradation between those electrolytes, commonly classed as weak, which obey Ostwald's Law at medium concentrations, but not at high ones, through the transition electrolytes,

which obey the Law at low concentrations, to the strong electrolytes, which do not obey the Law at all. It is impossible to say where one class ends and the other begins; and as we must assume the existence of non-ionised molecules in the solutions of weak electrolytes, and in the transition stage, it seems probable that there is no abrupt change in this capacity to form non-ionised molecules. In strong electrolytes, however, the proportion of these non-ionised molecules must be very much smaller than that given by conductivity measurements

$$\left(\frac{A_v}{A_\infty}\right).$$

The study of the Raman spectra (§ 397) of solutions of acids and salts throws some light on this question. The Raman effect is a molecular light scattering effect; each molecular species gives its own characteristic effect, and hence it is possible to find out whether non-ionised molecules (which would, of course, be a different molecular species from the ions) are actually present in solution. When examined in this way, both nitric and sulphuric acids are found to be only partially ionised in moderately concentrated and concentrated solutions. With the Raman effect, it is possible to follow the single-stage ionisation of nitric acid and the two-stage ionisation of sulphuric acid.

With regard to salts, with the exception of the anomalous mercuric chloride and mercuric cyanide, the Raman effect provides no evidence whatever for any undissociated molecules, even in the most concentrated solutions. By undissociated molecules is meant a molecular species in which the ions are bound together by a covalent bond of ordinary chemical strength.

The X-ray analysis of crystals of sodium and potassium chlorides, and of many other substances, has shown them to be ionised completely even in the solid state (§ 134). It would be unlikely for combination of ions to occur when the crystal was dissolved in water, though not impossible.¹ Rubens has shown that the reflection of infra-red rays by these crystals agrees with the assumption that they are completely ionised.

Further evidence can be obtained from consideration of distribution experiments. It has already been stated (§ 261) that distribution of the same molecular species occurs between two immiscible solvents, and if, by some reaction, or alteration in the molecular aggregation, this molecular species is altered, it is only the concentrations of the same molecular species which must be taken into account in calculating the distribution coefficient. Now, silver perchlorate is soluble in benzene, and gives a non-conducting solution. It is therefore not ionised. If

¹ It might be possible for the molecule to exist in aqueous solution with the electrovalent linkage between the ions unbroken; the ions would be held together by electrostatic forces, and the molecule, although ionised, would be undissociated.

water is shaken up with this benzene solution, the whole of the silver perchlorate is transferred to the aqueous layer. If any non-ionised molecules existed in the aqueous layer, there would be a distribution of them between the benzene and water. Hence, it is concluded that the molecular species formed in the aqueous layer are totally different from those in the benzene layer. Presumably the salt is completely ionised in the aqueous solution.¹ It must be pointed out, however, that many examples are known of the incomplete extraction of strong electrolytes from solutions in non-ionising solvents, and the only explanation of this is that there are non-ionised molecules of the electrolyte in the aqueous solution.

Evidence from vapour pressure observations depends upon the same application of the idea of distribution. Hydrogen chloride in aqueous solution has a very low vapour pressure of hydrogen chloride gas. According to Henry's Law (§ 233), the ratio of concentrations of the same molecular species between the gaseous and liquid phases is constant. The fact that the vapour pressure of the gas over the solution is so small was used as an argument for the theory of complete dissociation. The vapour pressure was much less than that required if the Arrhenius hypothesis were correct. But the fact that there is any vapour pressure of the gas at all over the solution indicates that there must, at least, be a very small concentration of non-ionised hydrogen chloride in the aqueous layer.

The conclusion to be drawn from this work is that although the Debye-Hückel theory is more near the truth than that of Arrhenius, its assumption that strong electrolytes are *completely* dissociated in solutions of moderate concentration is probably not true. Rather is it likely that a *very small* amount of the solute exists in the undissociated state.

322. Hydrogen Ion Concentration.—The most important ion is the hydrogen ion. Upon the concentration of hydrogen ions in a solution depends its acidic or alkaline properties (§ 326). The hydrogen ion is a powerful catalyst, and the whole course of a reaction may be modified by altering the hydrogen ion concentration in the medium in which the reaction takes place. A knowledge of hydrogen ion concentration is necessary in testing water, soil, and biological fluids, such as the blood.

The hydrogen ion concentration of a solution is usually expressed in a special way. The p_H of a solution is defined as the logarithm to the base 10 of the reciprocal of the hydrogen ion concentration in gm.-mols. per litre. Thus

$$p_H = -\log_{10} [H^+] = \log_{10} \frac{1}{[H^+]}$$

¹ It is, of course, possible that there might be solvated un-ionised molecules in the water layer, which would count as a separate molecular species from that of the solvated, or unsolvated, molecules in the benzene layer.

If the p_H of a solution is 4,

$$\log_{10} \frac{1}{[H^+]} = -\log_{10} [H^+] = 4,$$

and the hydrogen ion concentration is 10^{-4} , i.e., 0.0001 gm.-mol. per litre.

The student should make himself thoroughly familiar with this method of expressing hydrogen ion concentration. It has been adopted because it is frequently necessary to deal with very minute hydrogen ion concentrations, and these are conveniently expressed in this way.

It may be mentioned here that the hydrogen ion, in aqueous solutions, is invariably solvated, i.e., is attached to one or more molecules of water. It is usually supposed that one molecule of water is attached to each hydrogen ion, and the formula of the ion is, therefore, H_3O^+ , sometimes called the "hydroxonium" ion. Wherever the hydrogen ion (in aqueous solutions) is mentioned, the H_3O^+ ion is intended, but in order to simplify the work, the ion will be written H^+ .

323. The Calculation of Hydrogen Ion Concentrations in Acid Solutions.—An example will be taken at this point of the calculation of the p_H value of a solution, given the dissociation constant of the acid.

Thus, it is required to find the p_H value of a $N/100$ solution of acetic acid. The dissociation constant of the acid is 1.8×10^{-5} .

From the simplified form of Ostwald's Dilution Law, we have

$$\alpha = \sqrt{Kv}.$$

We can apply this because α is very small. Now, v is the volume containing 1 gm.-mol. of the acid, expressed in litres, i.e., in this case 100. Thus

$$\begin{aligned} \alpha &= \sqrt{100 \times 1.8 \times 10^{-5}} = \sqrt{1.8 \times 10^{-3}}, \\ &= 4.242 \times 10^{-2}. \end{aligned}$$

This value of α is the fraction of a gram-molecule dissociated. Hence, in 1 litre of solution there would be 4.242×10^{-4} gm.-mols. of hydrogen ions. The molecular concentration is 4.242×10^{-4} , and the $p_H = -\log [H^+]$

$$\begin{aligned} &= -(\bar{4}.6276) = -(-4 + 0.6276), \\ &= -(-3.3724), \\ &= 3.3724. \end{aligned}$$

Thus the p_H of the solution is 3.37.

Let us now find the p_H of a $N/1,000$ solution of acetic acid.

v is now 1,000. This time we will not assume α small. This means that instead of writing $\alpha = \sqrt{Kv}$ we must apply the Ostwald Dilution Law in the form

$$\frac{\alpha^2}{(1 - \alpha)v} = K,$$

Rearranging this gives a quadratic equation in a ;

$$a^2 + avK - vK = 0.$$

The roots of this are given by the expression

$$a = \frac{-vK \pm \sqrt{v^2K^2 + 4vK}}{2}$$

A negative root for a has no physical meaning and hence we can ignore the negative root and write

$$a = \frac{-vK + \sqrt{v^2K^2 + 4vK}}{2}$$

Substituting for v and K gives

$$a = \frac{-1.8 \times 10^{-2} + \sqrt{7.232 \times 10^{-2}}}{2}$$

$$= 1.26 \times 10^{-1}$$

Therefore in 1 litre of the solution there will be 1.26×10^{-4} g.-mols. of hydrogen ions.

$$\therefore p_H = -\log [H^+] = -\log (1.26 \times 10^{-4})$$

$$= 3.90$$

The p_H of an acid solution may be calculated in terms of a and the dissociation constant K as follows: Consider the ionic equilibrium in a solution of an acid HA at a concentration of C moles per litre. In this treatment we are assuming ideal conditions so concentration may be written for activity.

We apply the Law of Mass Action

$$\frac{[H^+][A^-]}{[HA]} = K$$

If a is the degree of dissociation, then $[A^-] = aC$ and $[HA] = C(1 - a)$.

Then

$$[H^+] = \frac{K[HA]}{[A^-]}$$

$$= \frac{KC(1 - a)}{aC}$$

$$= \frac{K(1 - a)}{a}$$

$$\frac{1}{[H^+]} = \frac{a}{K(1 - a)}$$

or,
$$p_H = \log_{10} \frac{1}{[H^+]} = \log_{10} \frac{1}{K} + \log_{10} \frac{a}{1 - a}$$

324. Methods of Determining Hydrogen Ion Concentration.—There are several methods of determining the hydrogen ion concentration of a solution. The chief are

- (1) The conductivity method.
- (2) The electromotive force method.
- (3) The freezing point method.
- (4) The colorimetric method.
- (5) The method of catalysis of ester hydrolysis.

(1) The conductivity method is simply that of determining the degree of dissociation of the acid. The degree of dissociation, α , is given by

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty},$$

where Λ_∞ and Λ_v are the equivalent conductivities at infinite dilution and at dilution v respectively. These can be determined by the method given in § 319. α is, of course, a direct measure of the hydrogen ion concentration.

(2) The electromotive force method, which is the most accurate method for determining hydrogen ion concentration will be dealt with in § 340.

(3) The freezing point method is only another way of determining the degree of dissociation, from which, of course, the p_H can be obtained. Knowing the true molecular weight of the acid, the molecular depression of the solvent used, and the depression of the freezing point caused by the solution of a known weight of acid in a given weight of solvent, α can be determined as previously indicated (§ 301).

(4) The colorimetric method. This depends on the use of indicators (§ 332). Only a brief indication of the application of the method will be given. Indicators are known which change their colour at various values of p_H , and, indeed, there is a universal indicator, a mixture of several indicators, which changes colour from purple, through blue, green, yellow, orange to red as the p_H changes in the direction of greater acidity. A series of buffer solutions is prepared (§ 330). A drop of the universal indicator is added to each of these, thus colouring each differently. The solution of unknown p_H is taken, a drop of the indicator is added, and the colour compared with that of the standards. In this way the tube matching with the unknown solution gives the p_H .

This is a satisfactory method where speed combined with moderate accuracy is required. There are indicator methods which do not involve the use of buffer solutions, but these do not yield such accurate results and are not so convenient.

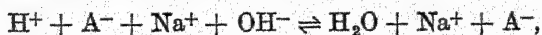
(5) The velocity of certain reactions (e.g., the hydrolysis of acetal) is directly proportional to the amount of hydrogen ion catalysing them. This can be used for the determination of hydrogen ion concentration.

325. The Ionisation of Water.—When hydroxyl ions and hydrogen ions are brought together, water is formed, which is practically undissociated. Water is very nearly an insulator, but the fact that the purest water will conduct the current a little points to the fact that it must be slightly broken down to its ions. The union of hydroxyl and hydrogen ions to form water is neatly shown by the ionic explanation of the fact that the heat evolved in the neutralisation of a strong acid by a strong base is always in the neighbourhood of 13,700 gm.-cals per gm.-mol. (§ 96). Thus, if hydrochloric acid and sodium hydroxide, in equivalent proportions in dilute solution, are mixed, there is an evolution of heat to the extent of 13,700 gm.-cals. per gm.-mol. The same is true for hydrochloric acid, and potassium hydroxide, and of nitric acid and a strong base. The following Table shows the heat of neutralisation of some of the commoner acids with sodium hydroxide.

TABLE LXXXVI

Acid.	Heat of Neutralisation.
	Gm.-cals. per gm.-mol.
Hydrochloric	-13,700
Nitric	-13,700
Hydriodic	-13,700
Hydrobromic	-13,800
Chloric	-13,800
Acetic	-13,400
0.5 gm.-mol. Sulphuric	-15,700
Hydrofluoric	-16,300

The fact that the heat of neutralisation per gm.-mol. of all these acids is about the same indicates that there must be a common reaction taking place for them all. If the ionic equation for an acid, say HA, reacting with sodium hydroxide is written, we have



since the salt formed will be well ionised. Thus, the net reaction is merely the union of hydrogen and hydroxyl ions to form the comparatively little dissociated water. This is the same with all strong acids and bases, particularly if the neutralisation is carried out in dilute solution, for then, the dissociation of the reactants is complete.

The ionisation of water is a reversible process. Hence, the Law of Mass Action will apply to it. Although water is but little ionised, this ionic equilibrium is one of the most important in physical chemistry, for it will explain many properties of aqueous solutions of electrolytes.

It is therefore of some interest to discover to what extent water is ionised. The usual method of finding the degree of dissociation is, of course, to determine the conductivity and calculate α from the result. Water conducts very feebly, and the presence of impurities makes a tremendous difference to the value obtained for the conductivity.

Kohlrausch and Heydweiller determined the specific conductivity of the purest distilled water and found it to be 0.0384×10^{-6} mhos at 18°C . We obviously cannot determine the equivalent conductivity at infinite dilution directly, but we can deduce the corresponding figure by adding the ionic conductances at infinite dilution of the hydrogen and hydroxyl ions (§ 305). The value for hydrogen is 313, and for hydroxyl 174 mhos. Hence, the equivalent conductivity of completely ionised water will be 487 mhos. The equivalent conductivity is equal to the conductivity multiplied by the volume in c.c. containing one gram-equivalent of the ions. Hence, the volume containing one gram-equivalent of hydrogen and hydroxyl ions

$$\begin{aligned} &= \frac{487}{0.0384 \times 10^{-6}} \text{ c.c.}, \\ &= 1.27 \times 10^{10} \text{ c.c.} \end{aligned}$$

Hence, the hydrogen ion concentration is

$$\begin{aligned} &\frac{1}{1.27 \times 10^{10}} \text{ gm.-equivs. per c.c.} \\ &= 0.78 \times 10^{-10} \text{ gm.-equivs. per c.c.} \\ &= 0.78 \times 10^{-7} \text{ gm.-equivs. per litre.} \end{aligned}$$

As stated above, the ionisation of water is a reversible process, and the Law of Mass Action can be applied to it. In the equilibrium



the amount of undissociated water is so great that its concentration may be regarded as constant. Hence,

$$[\text{H}^+][\text{OH}^-] = K_w.$$

K_w is the ionic product for water. Taking the figures obtained above,

$$K_w = 0.78 \times 0.78 \times 10^{-14} = 0.61 \times 10^{-14}.$$

This is the value at 18°C . The conductivity of pure water increases rapidly with the temperature, and the following Table shows the values of K_w at various temperatures.

$T^\circ \text{C}$	0	18	25	50	75	100	123	136	218
$K_w \times 10^{14}$	0.09	0.61	1.0	4.5	16.9	48	114	220	461

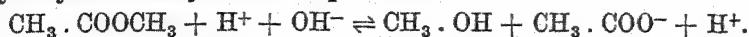
The value at 25°C . is usually taken as standard, because it is a convenient temperature for working and happens to give the value unity for the ionic product ($\times 10^{-14}$).

It is to be noted that K_w is the ionic product, and not the dissociation

constant of the reaction. The value of the latter at 18° C. would be given by

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{(0.78 \times 10^{-7})^2}{\left(\frac{1,000}{18}\right)} = \frac{1}{55} (0.78 \times 10^{-7})^2.$$

Another method of determining the concentrations of hydrogen and hydroxyl ions in water is that due to Wijs, who determined the rate of hydrolysis of methyl acetate in pure water.



It is clear that in this reaction, as it proceeds towards the right, the concentration of hydrogen ions increases, relative to that of the hydroxyl ions. It was shown that hydroxyl ions were much more effective catalysts for this hydrolysis than the hydrogen ions, being, in fact, about 1,400 times as active. The reaction velocity would therefore reach a minimum when the hydrogen ion concentration was 1,400 times as great as that of hydroxyl ions. From his results Wijs calculated that K_w was 1.44×10^{-14} , at 25° C.

The value of the ionic product has been determined by several other methods, and a list of the values obtained is given in the accompanying Table:—

TABLE LXXXVII.

Method.	K_w at 25° C.
Conductivity of pure water . . .	1.0×10^{-14}
Hydrolysis of sodium acetate . . .	1.15×10^{-14}
Hydrolysis of methyl acetate . . .	1.44×10^{-14}
E.m.f. of hydrogen-oxygen cell . . .	1.01×10^{-14}

There is thus little doubt of the order of this dissociation, and, for all ordinary purposes, the value of K_w is taken as 10^{-14} at 25° C.

Knowing the value of the ionic product, which is a multiple of the dissociation constant, at two different temperatures, we can calculate the heat of ionisation (ΔH) of water by making use of van't Hoff's equation (§ 114). This states that

$$\log_{10} K_1 - \log_{10} K_2 = \frac{-\Delta H}{4.576} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

Now, for $T_1 = 0^\circ \text{C.} = 273^\circ \text{Abs.}$, $K_1 = 0.09 \times 10^{-14}$

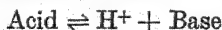
$T_2 = 50^\circ \text{C.} = 323^\circ \text{Abs.}$, $K_2 = 4.5 \times 10^{-14}$

$$\log(0.09 \times 10^{-14}) - \log(4.5 \times 10^{-14}) = \frac{-\Delta H}{4.576} \left(\frac{1}{273} - \frac{1}{323} \right)$$

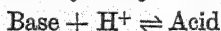
$$\begin{aligned}
 -1.6990 &= \frac{-\Delta H}{4.576} \left(\frac{50}{88,180} \right) \\
 \therefore \Delta H &= \frac{4.576 \times 1.6990 \times 8818}{5} \\
 &= 13,720 \text{ gm.-cals. per gm.-mol.}
 \end{aligned}$$

Now ΔH , the heat absorbed in ionisation, should be equal to the amount of heat given out when a strong base neutralises a strong acid in dilute solution if the theory is correct. It is seen that there is very satisfactory agreement between the calculated and observed values, which provides good evidence for the accuracy of the theories involved.

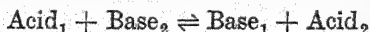
326. Acids and Bases.—The classical definition of an acid as a substance which gives hydrogen ions in water and of a base as one which gives hydroxyl ions in water is sufficient for a discussion of aqueous solutions. However, the definition will not serve for non-aqueous solutions. Brønsted and Lowry extended the classical definition by defining an acid as a substance with a tendency to lose a proton and a base as a substance with a tendency to gain a proton. The definition can be illustrated by the reaction scheme:



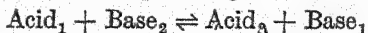
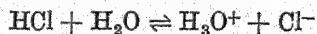
That is every acid has a base corresponding to it which differs only by containing one proton less than the acid. This base is known as the conjugate of the acid. Similarly every base has a conjugate acid thus



A free proton does not exist in solution,¹ so when an acid dissociates there must be molecules present that will take up the proton. This means that all acid base reactions will follow this scheme



Acid_1 and Base_1 are conjugate as are also Base_2 and Acid_2 . Consider an acid dissolved in a solvent; the dissociation of the acid will not take place unless the solvent can take up the protons given off by the acid. The solvent must have basic properties; thus the dissociation of hydrochloric acid in water involves the reaction:



A strong acid such as hydrochloric acid tends to lose its proton easily, and so the reaction will go mainly to the right-hand side of the equation. As a result the reverse reaction does not tend to proceed. The conjugate base Cl^- has little tendency to take up a proton and is, therefore, a weak base. This means that the conjugate base of a strong acid is

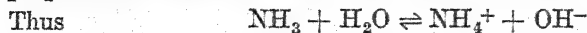
¹ It is more convenient in most discussions to write H^+ as though the free proton did exist. It should be remembered however, that the proton is always solvated (associated with a molecule of solvent). For example in dealing with aqueous solutions, H^+ is written though it would be more correct to write H_3O^+ .

weak; similarly the conjugate base of a weak acid, such as acetic acid, is strong. The dissociation of acetic acid is:



Here CH_3COO^- is the conjugate base of CH_3COOH . CH_3COO^- is quite a strong base; the dissociation reaction is largely reversed and as a result acetic acid is only slightly dissociated in water.

The reaction of a base in a solvent requires a solvent with acid properties in order to bring out the basic properties of the base.



Water can both supply and accept protons and is, therefore called an amphiprotic solvent. Alcohol behaves in a similar fashion. Solvents which accept protons are called protophilic; those which give up protons are called protogenic; and those which neither accept nor donate protons are called aprotic. Liquid ammonia is an example of a protophilic solvent. In liquid ammonia even a weak acid like acetic acid is highly ionised.⁹ Acetic acid is an example of a protogenic solvent; it will hinder the dissociation of even the strongest acids. On the other hand a protogenic solvent will assist the dissociation of a base.

In very strong protogenic solvents, for example hydrogen chloride, weak acids such as acetic acid, and even stronger acids, for example nitric acid, will behave as bases and accept protons from the solvent.

Assuming the concentration of water to be constant, then the equilibrium constant of the reaction



can be written

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$[\text{H}^+]$ can be substituted for $[\text{H}_3\text{O}^+]$ and so $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$. K_a is defined

therefore as it was in § 318. Similarly the dissociation constant of bases is not affected by the Brønsted-Lowry definition.

The strength of an acid is determined by its dissociation constant which measures its tendency to lose protons. While the strength of weak acids such as acetic acid can be measured in water, this is impossible for strong acids; the proton accepting power of water is such that all strong acids are completely ionised in water and their strengths cannot be distinguished. This effect is known as the levelling effect of a solvent.

In order to determine the strengths of the strong acids it is necessary to measure the dissociation in a protogenic medium. In such a solvent the ionisation of the acid is hindered. For example in acetic acid the equation for the dissociation of hydrochloric acid is

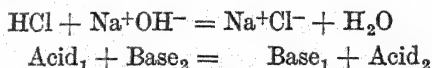


As the tendency of acetic acid is to lose a proton it will only accept a proton from a very strong acid. Measurements of dissociation constants in acetic acid medium show that perchloric acid HClO_4 is the strongest acid known and that the order of decreasing strength is

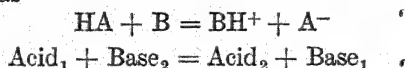


A solution of perchloric acid in acetic acid is a poor conductor, showing that even this acid is only weakly ionised in acetic acid. In a similar fashion the strengths of strong bases may be distinguished by using a protophilic solvent.

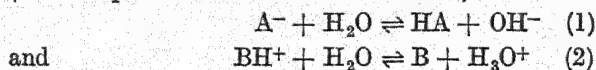
327. Neutralisation and Hydrolysis—Neutralisation is a reaction between equivalent amounts of an acid and a base. Consider, for example, the reaction:



This reaction as can be seen is an ordinary acid base reaction. Notice that the salt NaCl consists of the conjugate base of acid₁ (Cl^-) with the negative charge neutralised by a sodium ion. A neutralisation can be written generally as



In considering neutralisations we must take account of possible reactions between products of neutralisation and the solvent in which the neutralisation is being carried out. Two reactions are possible (water is presumed here to be the solvent)



These reactions are known as hydrolysis reactions if water is the solvent; in general they may be called solvolysis or lyolysis reactions. If HA is a strong acid then its conjugate base A will be weak and will not tend to take up a proton; therefore, hydrolysis reaction (1) will not proceed. If the original base B is strong then its conjugate acid BH is weak and has little tendency to lose a proton; hence the hydrolysis (2) will not take place. Hence hydrolysis is not important in a reaction involving the neutralisation of a strong base by a strong acid. If on the other hand HA is a weak acid then reaction (1) tends to proceed; if B is a weak base reaction (2) will proceed. The subject will now be discussed quantitatively.

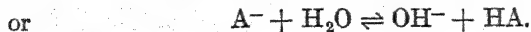
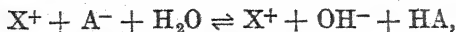
The strength of an acid or a base is measured by its dissociation constant (§§ 318, 326), so the extent of hydrolysis taking place will also depend upon this.

The degree of hydrolysis, h , is defined as the fraction of the total salt hydrolysed. Thus, if in a solution of aniline hydrochloride, $\text{C}_6\text{H}_5\text{NH}_2\text{HCl}$, 95 per cent. of the salt is hydrolysed into aniline and

hydrochloric acid, the degree of hydrolysis, h , is 0.95, or may be expressed as a percentage, 95 per cent.

The degree of hydrolysis can be calculated from the ionisation constants of the substances involved in the following way:—

The general reaction for the hydrolysis of the salt (XA) of a strong base and a weak acid is



Now $[A^-]$ represents the molecular concentration of unhydrolysed salt,

$[OH^-]$ represents the molecular concentration of free base,

and $[HA]$ represents the molecular concentration of free acid.

$$\therefore \frac{[OH^-][HA]}{[A^-]} = \frac{[\text{free base}][\text{free acid}]}{[\text{unhydrolysed salt}]} = K_h \quad (1)$$

the concentration of water being regarded as constant. K_h is called the *hydrolysis constant*, and it must be borne carefully in mind that it is not the degree of hydrolysis, although the latter can be obtained from it by calculation.

Now let $[H^+][OH^-] = K_w \quad (2)$

and $\frac{[H^+][A^-]}{[HA]} = K_a \quad (3)$

where K_w is the ionic product for water, and K_a is the dissociation constant of the acid.

Dividing (2) by (3), we have

$$\frac{[OH^-][HA]}{[A^-]} = \frac{K_w}{K_a} = K_h.$$

Thus the hydrolysis constant, K_h , is the ratio of the ionic product for water to the dissociation constant, K_a , of the weak acid.

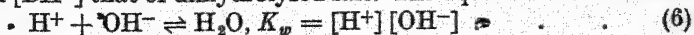
The equation in the case of the salt ($BH^+ A^-$) of a strong acid and a weak base¹ is derived in a similar way. In this case the general equation is



Applying the Law of Mass Action, we have

$$\frac{[H^+][B]}{[BH^+]} = K_b \quad (5)$$

the concentration of water being regarded as constant. Now $[H^+]$ represents the molecular concentration of the free acid, $[B]$ that of free base, and $[BH^+]$ that of unhydrolysed salt. The equilibria involved are



and $\frac{[BH^+][OH^-]}{[B]} = K_b \quad (7)$

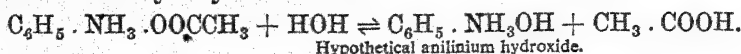
¹ Examples of such salts are the amine hydrochlorides: $RNH_3^+ Cl^-$.

Dividing (6) by (7), we get

$$\frac{[B][H^+]}{[BH^+]} = K_h = \frac{K_w}{K_b} \quad (8)$$

Thus, in the case of the salt of a weak base and a strong acid, the hydrolysis constant is the ratio of the ionic product for water to the dissociation constant of the weak base.

A very similar method of treatment leads to the relationship for the case of a *salt of a weak acid and a weak base*. Take, for example, aniline acetate. This hydrolyses as follows:—



If we assume that the salt is completely ionised, we have
 $C_6H_5NH_3^+ + CH_3 \cdot COO^- + H \cdot OH \rightleftharpoons C_6H_5 \cdot NH_3 \cdot OH + CH_3 \cdot COOH$;
 or, in general,



$$\therefore \frac{[BHOH][HA]}{[BH^+][A^-]} = K_h \quad (9)$$

The equilibria involved are:—

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (10)$$

$$K_b = \frac{[OH^-][BH^+]}{[BHOH]} \quad (11)$$

$$K_w = [H^+][OH^-] \quad (12)$$

$$\therefore \frac{K_w}{K_a \cdot K_b} = \frac{[H^+][OH^-][HA][BHOH]}{[H^+][A^-][OH^-][BH^+]} = \frac{[HA][BHOH]}{[BH^+][A^-]} = K_h$$

We can sum up these results as follows:—

For the salt of a *weak acid*, and a *strong base*, $K_h = \frac{K_w}{K_a}$.

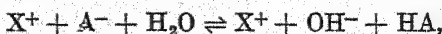
For the salt of a *weak base* and a *strong acid*, $K_h = \frac{K_w}{K_b}$.

For the salt of a *weak acid* and a *weak base*, $K_h = \frac{K_w}{K_a K_b}$.

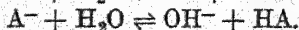
Notice that it is always the dissociation constant of the weak constituent that appears in the denominator.

These formulae can only be regarded as approximately true, for they have been derived on the basis of assumptions which are probably in part inaccurate.

The relationship between K_h and h follows from consideration of equation (1), above. We have for the equation for the hydrolysis of a salt of a strong base and a weak acid



or



If one gram-molecule of the salt is dissolved in v litres of water, and h is the degree of hydrolysis, the molecular concentration of unhydrolysed salt is $\frac{1-h}{v}$, and that of the hydrolysed salt and of the free acid will

be $\frac{h}{v}$.

$$\text{Hence, } K_h = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} = \frac{h^2}{v(1-h)}.$$

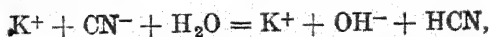
If h is small, $vK_h = h^2$.

As an example of the use of the above equations, we will calculate the degree of hydrolysis of $N/10$ and $N/100$ solutions of potassium cyanide. The dissociation constant of hydrogen cyanide is 7.2×10^{-10} at 25°C .

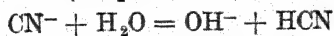
Potassium cyanide is the salt of a strong base and a weak acid,

$$\therefore K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{7.2 \times 10^{-10}} \\ = 1.389 \times 10^{-5}.$$

Now, the reaction is



or



and

$$K_h = \frac{[\text{OH}^-][\text{HCN}]}{[\text{CN}^-]}.$$

The degree of hydrolysis is h . In $N/10$ solution $[\text{OH}^-] = \frac{h}{10} = [\text{HCN}]$

and $[\text{CN}^-] = \frac{1-h}{10}$.

$$\therefore \frac{\frac{h^2}{100}}{\frac{1-h}{10}} = K_h = 1.389 \times 10^{-5}$$

$$\frac{h^2}{1-h} = 1.389 \times 10^{-4}$$

h will be small and can be neglected with respect to 1.

$$\therefore h^2 = 1.39 \times 10^{-4}$$

$$h = 1.18 \times 10^{-2}.$$

In $N/100$ solution, $[\text{OH}] = \frac{h}{100} = [\text{HCN}]$, and $[\text{CN}^-] = \frac{1-h}{100}$.

$$\therefore \frac{\frac{h^2}{10,000}}{\frac{1-h}{100}} = 1.389 \times 10^{-5}$$

$$\frac{h^2}{1-h} = 1.389 \times 10^{-3}.$$

Neglecting h with respect to 1, we have

$$h^2 = 1.39 \times 10^{-3}$$

$$\therefore h = 3.77 \times 10^{-2}.$$

323. Determination of the Degree of Hydrolysis of a Salt.—There are several methods of doing this, including the following:—

- (1) The Distribution Method.
- (2) The Conductivity Method.
- (3) The Colligative Property Method.
- (4) Hydrogen Ion Methods.

(1) *The Distribution Method.*—It is obvious that the ordinary methods of chemical analysis cannot be used to investigate the equilibrium, for this would be shifted by their application. A physical method must therefore be used. In the distribution method, a solvent is taken which will dissolve one of the products of the hydrolysis. The distribution of this substance between the solvent and water is first determined, so that the concentration of the substance in the solvent, if subsequently determined, is an index of the concentration in the aqueous layer.

The degree of hydrolysis of aniline hydrochloride may be found in this way. First it is necessary to determine the distribution coefficient of aniline between water and benzene. This is done by shaking 10 gms. of aniline with 1,000 c.c. of water and 60 c.c. benzene. Withdraw 50 c.c. from the benzene layer, and determine the amount of aniline in it by passing in dry hydrogen chloride gas. This precipitates the aniline as hydrochloride, in which form it may be weighed by evaporating off the excess of benzene on the water bath. From the weight of the hydrochloride, the weight of aniline in the benzene layer can be found. The rest must be in the water layer. Taking the volume of the benzene layer as 59 c.c., allowing 1 c.c. for solution in water, the concentrations of aniline in the two layers are found, and the distribution coefficient determined.

Now take 10 gms. of aniline hydrochloride (or the equivalent of aniline and hydrochloric acid) and shake up as before with 60 c.c. benzene and 1,000 c.c. water. Determine the amount of aniline in the benzene layer by precipitation with dry hydrogen chloride. From the distribution coefficient we know the weight of free aniline in the aqueous layer, and from this the degree of hydrolysis can be found.

Let D be the distribution coefficient of the aniline between benzene and water, and v the volume of benzene, in litres, taken to 1,000 c.c. water.

Let c_1 be the concentration of base in the aqueous layer, in gram-

equivalents per litre, and c_2 the original concentration of the salt in gram-equivalents per litre.

As there is c_1 of base in the aqueous layer, there must also be $c_1 vD$ in the benzene layer, so that the total concentration of the base is $c_1(1 + vD)$. Hence, the concentration of the unhydrolysed salt is $c_2 - c_1(1 + vD)$. There must also be, in the aqueous layer, acid of concentration $c_1(1 + vD)$.

Applying the Law of Mass Action to the equilibrium



$$\frac{[\text{base}][\text{acid}]}{[\text{salt}]} = K_h.$$

Substituting the values found, we have

$$\frac{c_1^2(1 + vD)}{c_2 - c_1(1 + vD)} = K_h,$$

from which K_h can be readily calculated. The degree of hydrolysis can be calculated from this.

(2) *The Conductivity Method.*—Suppose a solution contains one gram equivalent of salt per litre and that h is the degree of hydrolysis, then the concentration of unhydrolysed salt is $1 - h$ and there are h gram equivalents of free base and free acid also present. The acid is assumed weak, and therefore, un-ionised. Hence it is assumed that it does not contribute to the conductivity of the solution. The conductivity is therefore

$$\Delta = (1 - h) \Delta' + h \Delta''$$

and so

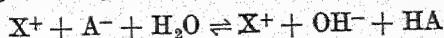
$$h = \frac{\Delta - \Delta'}{\Delta'' - \Delta'}$$

where Δ' is the equivalent conductivity of the unhydrolysed salt and Δ'' the equivalent conductivity of the free base. The conductivity Δ can be measured. Δ'' is usually taken as the equivalent conductance of the base at infinite dilution (this assumes the concentration of base is small). Δ' is determined by adding free acid to the solution. Since

$K_b = \frac{[\text{free base}][\text{free acid}]}{[\text{unhydrolysed salt}]}$, to maintain the equilibrium the addition of

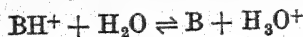
free acid must result in an increase in the amount of unhydrolysed salt. Thus, the hydrolysis decreases. By adding sufficient free acid the hydrolysis can be repressed. The free acid is therefore added to the solution until the conductivity becomes constant, which means that the hydrolysis has been completely repressed, and the conductivity of the solution Δ' is now assumed to be entirely due to unhydrolysed salt. It is assumed that the free acid does not contribute to the conductivity. On finding Δ , Δ' and Δ'' , h can be determined. The chief error in the method lies in the neglect of the conductance of the added acid.

(3) *The Colligative Property Method.*—In the equation



there is obviously an increase in the number of individuals present, water not being counted. This will result in a lowering of the vapour pressure, and hence a lowering of freezing point and elevation of boiling point. By determining the effect of the hydrolysis on one of these we can find the degree of hydrolysis. Since these methods are not very sensitive, it is clear that they can only be used with accuracy for substances that are highly hydrolysed.

(4) *Hydrogen Ion Methods.*—As an example, suppose that a solution containing x gram-molecules of the salt of a strong acid and a weak base, dissolved in 1 litre of water, is investigated. The p_H of this solution is found to be 5.8, say. It is required to find the degree of hydrolysis. The equation governing the hydrolysis is



If h is the degree of hydrolysis, the amount of BH^+ left will be $x(1 - h)$, and the amounts of B and H_3O^+ formed will be xh . The concentration of hydrogen ions may be found from the p_H value as follows:—

$$-\log_{10} [H^+] = 5.8,$$

$$\log_{10} [H^+] = -5.8000$$

$$[H^+] = 1.585 \times 10^{-6} \text{ gm.-mols. per litre.}$$

Hence $xh = 1.585 \times 10^{-6}$ gm.-mols. per litre. Knowing x , h can be calculated.

Having determined x and h , K_h can be determined. Further, for a weak acid and strong base the same method can be applied if the concentration of OH^- ions in solution is determined. Therefore, the hydrolysis constant for any reaction can be determined once the p_H of the solution is found. Any method of determining p_H can be used, for example indicators or electromotive force methods. The fact that H^+ or OH^- ions may be specific catalysts for certain reactions and that the velocity of these reactions is proportional to the concentration of catalytic ion has also been used to determine the p_H of solutions in which salts are hydrolysed.

329. Determination of the Ionic Product for Water from Consideration of Hydrolysis.—For the hydrolysis of the salt of a weak acid and a strong base the value of the hydrolysis constant, K_h , is given by

$$K_h = \frac{K_w}{K_a}$$

If we can find K_h and K_a we can obviously find K_w , provided that the method used for finding K_h does not involve the use of K_w .

As an example, we can take the hydrolysis of sodium acetate. For a

M/10 solution at 25° C., the hydrolysis amounts to 0.008 per cent.

$$\therefore [\text{acid}] = [\text{base}] = 0.00008 \times 0.1$$

[salt] = 0.1 (neglecting the very small amount hydrolysed)

$$\therefore K_h = \frac{[\text{acid}][\text{base}]}{[\text{unhyd. salt}]} = \frac{(0.000008)^2}{0.1} = 0.64 \times 10^{-9}.$$

Now K_a for acetic acid = 1.8×10^{-5} .

$$\therefore K_w = K_a K_h = 1.8 \times 10^{-5} \times 0.64 \times 10^{-9} \\ = 1.2 \times 10^{-14}$$

$$\text{i.e., } [\text{H}^+][\text{OH}^-] = 1.2 \times 10^{-14},$$

$$\text{or } [\text{H}^+] = [\text{OH}^-] = 1.1 \times 10^{-7}$$

330. Buffer Solutions.—Even the purest water does not retain a p_H value of 7 for very long. The reason for this is that carbon dioxide in the air dissolves in the water and gives it a slight acid reaction, or silicates may be dissolved from the glass in which the water is kept, and the smallest trace of these impurities gives rise to an alteration in the p_H value. It is sometimes necessary to prepare solutions of known p_H value, and to know that this p_H will not alter when, say, a drop of indicator is added to the solution. Such solutions, which are reasonably permanent in p_H value, are called solutions with reserve acidity or alkalinity, or more often *buffer solutions*.

Buffer solutions are usually made up of a mixture of the salt of a weak acid and the acid itself in various proportions, e.g., sodium acetate and acetic acid. In a solution of this mixture we have mainly sodium ions and acetate ions. There will also be some hydrogen and hydroxyl ions. There is, however, a large excess of acetate ions owing to the presence of the well-ionised sodium acetate. If hydrogen ions are added to this solution they combine with the acetate ions to give very slightly dissociated acetic acid



$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K.$$

A^- stands for the acetate ion.

Hence there will be little increase in the p_H . The addition of an acid to the buffer solution therefore makes little difference to the p_H value.

The value of the p_H for a mixture of sodium acetate and acetic acid can easily be calculated if the dissociation constant of the acid is known.

Thus, the dissociation constant of acetic acid is 1.8×10^{-5} at 25° C. Suppose we have a solution containing 0.2 gm.-molecule of acetic acid per litre, and 0.02 gm.-molecule of sodium acetate per litre. We require to find the p_H of the solution.

We have

$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = 1.8 \times 10^{-5},$$

or

$$[\text{H}^+] = \frac{1.8 \times 10^{-5} \times [\text{HA}]}{[\text{A}^-]}.$$

Assuming that the acid, since it is weak, is not dissociated at all, whilst the salt is completely dissociated,

$$[\text{HA}] = 0.2,$$

$$[\text{A}^-] = 0.02.$$

$$\therefore [\text{H}^+] = 1.8 \times 10^{-5} \times 10 = 1.8 \times 10^{-4}$$

$$p_{\text{H}} = + \log_{10} \frac{1}{[\text{H}^+]} = 3.74.$$

If the solution contains 0.02 gm.-molecule of acetic acid, and 0.2 gm.-molecule of sodium acetate, we can calculate the p_{H} in a similar way.

As before,

$$[\text{H}^+] = \frac{1.8 \times 10^{-5} \times [\text{HA}]}{[\text{A}^-]}$$

$$[\text{H}^+] = \frac{1.8 \times 10^{-5} \times 0.02}{0.2}$$

$$= 1.8 \times 10^{-6}$$

$$\therefore p_{\text{H}} = + \log_{10} \frac{1}{[\text{H}^+]} = 5.74.$$

The values of the p_{H} given in the Table below have been obtained by calculation in this way:—

TABLE LXXXVIII

Gm.-mol. Acetic Acid per Litre.	Gm.-mol. Sodium Acetate per Litre.	p_{H}
0.185	0.015	3.6
0.164	0.036	4.0
0.126	0.074	4.4
0.080	0.120	4.8
0.042	0.158	5.2
0.019	0.181	5.5

These values can be plotted, and the amount of each substance required to give a certain p_{H} can be calculated (Fig. 201).

In the calculation above we assumed that as the dissociation of the acid was small $[\text{A}^-]$ is equal to the concentration of the salt in solution and $[\text{HA}]$ is the concentration of acid put into the solution.

The expression for $[H^+]$ involves the ratio $[HA]$ to $[A^-]$ and p_H involves the inverse ratio, $[A^-]$ to $[HA]$, that is the ratio of salt to acid. Dilution of a buffer solution does not change this ratio and hence dilution leaves the p_H of the buffer unaffected.

The expression
$$[H^+] = \frac{K [HA]}{[A^-]}$$

can be rearranged to
$$\frac{1}{[H^+]} = \frac{[A^-]}{K[HA]}$$

hence
$$p_H = \log_{10} \frac{1}{[H^+]} = \log_{10} \frac{1}{K} + \log_{10} \frac{[Salt]}{[Acid]}$$

The expression $\log_{10} \frac{1}{K}$ is known as the p_K of the acid. The equation

$$p_H = p_K + \log \frac{[salt]}{[acid]}$$
 is called the Henderson equation.

It is clear that a solution containing the salt of any weak acid together with the weak acid itself will behave in a similar way to the above, and the following are frequently used as buffer solutions:

Sodium carbonate and sodium bicarbonate.

Disodium hydrogen phosphate and sodium dihydrogen phosphate.

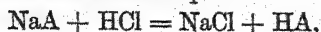
Boric acid and borax.

Citric acid and sodium citrate.

Phthalic acid and potassium hydrogen phthalate.

The effect of adding 1 c.c. of $N/100$ hydrochloric acid to 1 litre of the buffer solution containing 0.2 gm.-molecule of acetic acid per litre and 0.02 gm.-molecules of sodium acetate per litre, of which the p_H has just been found, may be calculated.

The amount of hydrochloric acid added is 0.00001 gm.-molecule. Assuming the acid to be completely dissociated, 0.00001 gm.-molecule of hydrogen ion will be added. The volume change consequent upon the addition will be neglected. The addition of the hydrogen ions causes the formation of more acetic acid from the sodium acetate, and some of the latter will be used up:—



where A stands for the acetate group. Assuming that the acetic

acid is not at all dissociated and the sodium acetate is completely dissociated, the reaction will proceed to completion, and all the hydrogen

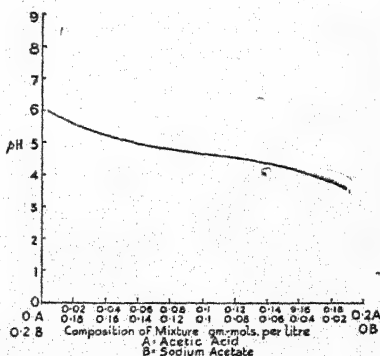


FIG. 201.— p_H Values of Mixtures of Sodium Acetate and Acetic Acid.

ions will be used up in forming undissociated acetic acid. The amount of undissociated acid thus formed will be 0.00001 gm.-molecule, and the amount of sodium acetate used up will also be 0.00001 gm.-molecule, so that the concentrations $[HA]$ and $[A^-]$ are now 0.20001, and 0.01999 gm.-molecule respectively. Hence, as explained above,

$$\begin{aligned} [H^+] &= \frac{1.8 \times 10^{-5} \times [HA]}{[A^-]} \\ &= \frac{1.8 \times 10^{-5} \times 0.20001}{0.01999} \\ &= 1.801 \times 10^{-4}, \end{aligned}$$

giving a p_H of $\log_{10} \frac{1}{1.801 \times 10^{-4}} = 3.74$, which is not different from that of the buffer solution itself (3.74, calculated above).

The effect of adding 1 c.c. of $N/100$ hydrochloric acid to water is much greater. The concentration of $[H^+]$ added is 0.00001 gm.-molecule per litre. Neglecting the ionisation of water, the p_H of this solution would obviously be $\log_{10} \frac{1}{10^{-5}} = 5$. The p_H therefore changes from 7 to 5.

The above calculations on the p_H of buffer solutions have been very greatly simplified. The assumptions with regard to the degree of dissociation of the weak acid and its salt are certainly not true; but, without this simplification, the calculation is very complicated.

Buffer solutions also resist change in p_H on the addition of alkali. For example when sodium hydroxide is added to a sodium acetate-acetic acid mixture the acetic acid reacts with sodium hydroxide to form water and sodium acetate. The OH^- ions of the base are thus removed from the solution leaving the p_H of the buffer relatively undisturbed. Buffer solutions are also made up from mixtures of weak bases and their salts. The principle of the buffering action of such solutions is the same as for the weak acid-salt mixtures.

331. Hydrogen Ion Concentration Changes in the Neutralisation of a Strong Acid by a Strong Base.—Quite a different state of affairs is met with here, because the acid, the base, and the salt may all be regarded as completely ionised.

Let us consider the titration of a normal solution of a base with a normal solution of a strong acid, and calculate the p_H of the solution at various stages in the neutralisation. Since both acid and base are strong, there will be no effect on the salt produced during the neutralisation, and no hydrolysis.

When 10 c.c. of acid have been added to 50 c.c. of base, and the whole has been made up to 1 litre, there are 40 c.c. of base left. Since the solution was normal there are 40/1,000 gm.-equivalents of base in this volume, so the hydroxyl ion concentration now is 40/1,000, i.e., $0.04 =$

4×10^{-2} . The hydrogen ion concentration is given by the expression

$$[H^+][OH^-] = 10^{-14}.$$

Hence,
$$[H^+] = \frac{10^{-14}}{4 \times 10^{-2}} = 2.5 \times 10^{-13}.$$

When 20 c.c. of acid have been added, there are now 30 c.c. of base left un-neutralised, and hence the hydroxyl ion concentration is now 3×10^{-2} , and the hydrogen ion concentration 3.3×10^{-13} .

The p_H begins to alter very rapidly in the neighbourhood of the neutralisation point. When 49.5 c.c. of acid have been added, there is 0.5 c.c. of base left, and the hydroxyl ion concentration is $0.5/1,000 = 5 \times 10^{-4}$. The hydrogen ion concentration is

$$10^{-14} \div 5 \times 10^{-4} = 2 \times 10^{-11}.$$

Now, when 50.5 c.c. of acid have been added, the hydrogen ion concentration is 5×10^{-4} . There is thus a change in hydrogen ion concentration from 2×10^{-11} to 5×10^{-4} during the addition of 1 c.c. of acid at the neutralisation point. Obviously such a mixture could not be used as a buffer mixture, because the addition of a trace of acid would alter its p_H very much.

The values obtained for the p_H of the solution at various points in the titration are given in the Table LXXXIX, and are also plotted in the graph (Curve I). This curve is a typical neutralisation curve for a strong acid and a strong base.

This curve should be compared with that for the titration of a weak acid by a strong base (Curve II).

The calculation in this case is rather more difficult owing to the fact that the acid is only slightly dissociated, the salt produced by the

TABLE LXXXIX.

Cc. N NaOH added to 50 c.c. N acid.	$[H^+]$	p_H
45.0	5×10^{-3}	2.3
49.0	1×10^{-3}	3.0
49.5	5×10^{-4}	3.3
49.9	1×10^{-4}	4.0
49.95	5×10^{-5}	4.3
50.0	1×10^{-7}	7.0
50.05	2×10^{-10}	9.7
50.10	1×10^{-10}	10.0
50.5	2×10^{-11}	10.7
51.0	1×10^{-11}	11.0
55.0	2×10^{-11}	11.7

neutralisation depresses the dissociation of the acid, and the salt is hydrolysed. All three factors have to be taken into account in deducing a mathematical expression for the p_H at any given stage of the neutralisation. In the addition of an alkali to a weak acid, there will be a comparatively large effect on the p_H at first, owing to the combination of the few hydrogen ions present with the added hydroxyl ions of the alkali, but the curve soon flattens out as the salt produced represses the ionisation of the acid. At the equivalence point there is a sudden rise, the sharpness of which will depend upon the degree of hydrolysis of the salt formed. The weaker the acid, the greater the hydrolysis, and the smaller the inflexion of the curve. For a very weak acid, the p_H changes gradually over the whole range. The titration curve is shown in Fig. 202 for the case of a moderately weak acid (II) and a very weak acid (III) and a strong base.

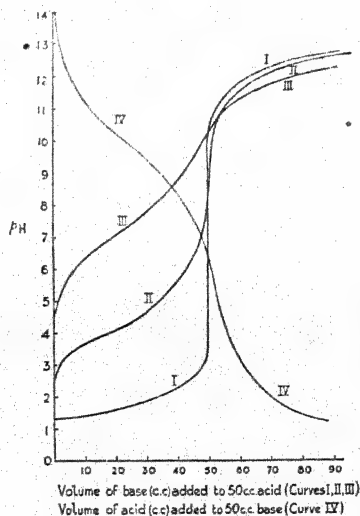


FIG. 202.—Titration of an Acid with a Base.

- | | |
|-----------------------------|----------------------------------|
| I. Strong acid—strong base. | III. Very weak acid—strong base. |
| II. Weak acid—strong base. | IV. Weak base—strong acid. |

These curves are of importance in connection with electrometric titrations (§ 340). It is clear that the sudden change of p_H for a strong acid and a strong base indicates the end-point of the reaction. Methods of finding p_H values are given in § 324; the one usually employed for this work is the e.m.f. method. It is obvious that the lack of a sudden change in p_H in the case of a weak acid being neutralised by a strong base makes this method of little value in this instance. The curve for a weak base titrated with a strong acid is similar to the Curve II, but starts in the top left-hand corner and finishes at the bottom right-hand corner (Curve IV).

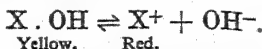
332. Theory of Indicators.—An indicator is a substance which possesses one colour in acid solution and an entirely different one in alkaline solution, *i.e.*, its colour changes with changing hydrogen ion concentration. It follows that it will be more sensitive the smaller the pH range over which the colour changes.

Ostwald's theory of indicators (1891) supposed that the colour change was due to ionisation. Indicators were supposed to be weak acids or weak bases. They dissolved to give small amounts of hydrogen or hydroxyl ions, and their degrees of ionisation were altered by changes in the concentration of these ions. It was assumed that in the non-ionised state the indicator had a different colour from that of its ions.

Suppose that the indicator is a weak acid HX . It dissociates in water according to the equation

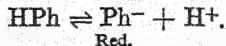


Addition of hydrogen ions causes the reaction to go from right to left. The hydrogen ion is, of course, colourless, and so it must be the X^- ion that is coloured. Let us see what happens in the case of methyl orange. Methyl orange was supposed by Ostwald to be a very weak base. In solution, therefore, there will be traces of hydroxyl ions and a cation. The undissociated substance is yellow; the colour of the cation is red. The methyl orange dissociates as follows:—



Addition of acid forces the ionisation towards the right, for the hydrogen ions combine with the hydroxyl ions to give the relatively little ionised water. This results in the further ionisation of the indicator, and the liquid is consequently red. On adding alkali, hydroxyl ions are added, which force the ionisation back to the left. Hence, the solution becomes yellow.

Phenolphthalein may be supposed to act as a weak acid. It therefore dissociates as follows:—



The undissociated acid is colourless; the Ph^- ion is red. Addition of hydrogen ions, *i.e.*, addition of acid, forces the dissociation back, and causes the formation of undissociated phenolphthalein which is colourless. Addition of OH^- ions (*i.e.*, addition of alkali) causes diminution of the hydrogen ion concentration, and therefore further ionisation takes place. The colour is thus that of the Ph^- ion, *i.e.*, red.

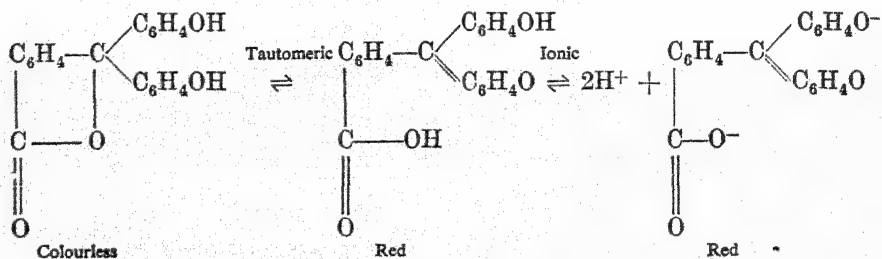
The fact that phenolphthalein cannot be satisfactorily used for the titration of ammonia or other weak bases is due to the hydrolysis of the salt formed between the ammonia and the indicator. Near the end-point of the titration there would be formed some NH_4Ph , but hydrolysis prevents the formation of Ph^- ions as shown in the equation



Hence, the solution remains colourless until a large excess of ammonia has been added.

Methyl orange, being a weak base, is, in a similar way, unsuitable for the titration of a weak acid, but quite satisfactory for a weak base. This point is also brought out by a study of the titration curves (Fig. 202) for a strong acid and a weak base, and a weak acid and a strong base. The indicator works only over a certain p_H range (Table XC). This range may cover the addition of a large quantity of one of the reactants to the other. Thus, in Curve III, the p_H changes from 5 to 8 during the addition of several c.c. of base, and an indicator changing colour over this range would not give a satisfactory end-point. In Curve I, this p_H change occurs with the addition of a few drops of base only, and hence an indicator changing colour over this range could be used satisfactorily.

It is now generally regarded that the cause of the colour changes of indicators is a tautomeric change in structure rather than ionisation. It is supposed that an indicator solution consists of an equilibrium mixture of two or perhaps more tautomers, one of which exists in acid solution, the other in alkaline solution. At least one of the tautomers is a weak acid or a weak base. Phenolphthalein is a "pseudo-acid". Its salts have the same structure as the acid itself, whilst colourless phenolphthalein is not an acid. The two forms of phenolphthalein are



It can readily be understood how phenolphthalein acts as an indicator on the basis of this theory. Let H_2Ph be the colourless phenolphthalein,¹ and H_2Ph the tautomeric coloured form. When sodium hydroxide is added, the salt $\text{Na}_2\text{Ph}'$ is formed, which is coloured, as the Ph^- ion is red, and the Na^+ ion is colourless. So long as the solution is acid, there is no formation of red ions, as the form H_2Ph alone exists in the solution.

It follows from the relationship between p_H and dissociation constant of an acid (§ 326)

$$p_H = \log_{10} \frac{1}{K} + \log_{10} \frac{\alpha}{1 - \alpha},$$

that if $\alpha = 0.5$, $p_H = \log_{10} \frac{1}{K}$.

¹ Phenolphthalein is probably a dibasic acid, as shown.

TABLE XC.—COLOUR CHANGES OF INDICATORS

Indicator \ pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Crystal Violet	Green	Green-blue	Blue	Violet											
Cresol Red.	Red		Yellow					Yellow		Red					
Bromophenol Blue		Yellow			Blue										
Methyl Orange				Red			Yellow								
Methyl Red				Red			Yellow								
p-Nitrophenol							Green	Yellow							
Bromothymol Blue							Yellow		Blue						
Litmus					Red	Red-violet	Violet	Violet	Blue-violet	Blue					
α -Naphtholphthalein								Yellow		Blue					
Phenolphthalein								Colourless		Rose	Red				
Thymolphthalein										Colourless		Blue			
Nitramine											Colourless		Orange-brown		
Trinitrobenzene												Colourless	Orange	Red	

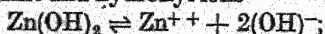
When the indicator is half converted from the form existing in acidic to that in basic solutions $[H^+] = K$. This relationship is extremely useful, and is the basis of the determination of the p_H of a solution, whilst it may also be used for the determination of the degree of dissociation of an indicator.

Table XC gives the colour changes of a number of indicators and shows their working range.

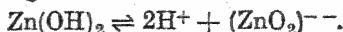
The choice of an indicator for any particular reaction depends largely upon the nature of the p_H neutralisation curve (Fig. 202). In the titration of a strong acid with a strong base (Curve I), the point of exact equivalence is at $p_H 7$, but the change from $p_H 4$ to $p_H 10$ and *vice versa* is brought about by the existence of as small a quantity as 0.1 c.c. of acid and base respectively in excess. Hence, any indicator changing in colour within the p_H range 4 to 10 could be used without introducing serious error. Even if it changed at $p_H 4$, the error would only be 0.1 c.c. Consider now the case of the titration of a weak acid by a strong base, e.g., acetic acid by sodium hydroxide. This is typified by Curve II. Actually, sodium acetate is hydrolysed to a certain extent, and, when the p_H of the solution is 7, the point of equivalence has not been reached. The p_H of the solution of sodium acetate is nearly 9. The inflexion of the curve is not so sharp as in Curve I, so that if an indicator were chosen which changes, say, at $p_H 4$ (e.g., methyl orange), this would be considerably in error. Owing to the broad inflexion, the p_H limits for an error of 0.1 c.c. on the acidic or basic side are reduced to about 8 and 10. An indicator changing over this range (e.g., phenolphthalein, changing at $p_H 9$) would have to be used. For the titration of a weak base by a strong acid (Curve IV), the inflexion is broad, and, owing to hydrolysis, the point of equivalence will lie on the acid side. To secure an accuracy of 0.1 c.c. on either side, an indicator changing within the range $p_H 3$ to 5 must be used.

333. Amphoteric Electrolytes, or Ampholytes.—An amphoteric substance is one which behaves either as an acid or as a base, according to the circumstances. In other words, it can either supply or take up protons.

Many inorganic substances are amphoteric. Common examples are zinc hydroxide, $Zn(OH)_2$, aluminium hydroxide, $Al(OH)_3$, and stannous hydroxide, $Sn(OH)_2$. These amphoteric hydroxides are capable of forming salts with both acids and bases. Thus, zinc hydroxide combines with dilute sulphuric acid to give zinc sulphate, which gives a metallic cation. It also dissolves in sodium hydroxide solution, giving sodium zincate, Na_2ZnO_2 , in which the metal is to be found in the anion. It is to be supposed that, although the ionisation of zinc hydroxide is very small, it can take place in two ways, according to the circumstances. Thus, it may give zinc and hydroxyl ions

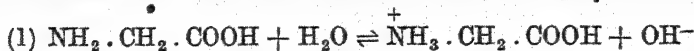


or it may give hydrogen ions and zincate ions



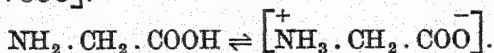
Suppose an alkali is added to a suspension of zinc hydroxide in water. In this case, the second type of ionisation will be favoured, since hydrogen ions will be removed from the sphere of action by combination with hydroxyl ions to form water. Thus, the formation of zincate ions will proceed almost to completion. If, however, an acid is added to the suspension of zinc hydroxide in water, the first type of ionisation will be favoured, as hydroxyl ions will be removed by the added hydrogen ions. In the amphoteric hydroxides, it is really the hydroxyl group which is capable of ionising in two ways.

Many organic substances are also amphoteric, but here the amphoteric nature is due to a different cause. Organic ampholytes contain two different groups, one being acidic and the other basic in nature. The most common example of such a compound is an amino-acid, such as glycine (amino-acetic acid), $\text{CH}_2\text{NH}_2\text{COOH}$. The $-\text{NH}_2$ group has basic powers, the $-\text{COOH}$ group has acidic powers. The substance can, therefore, ionise in two ways in aqueous solution.

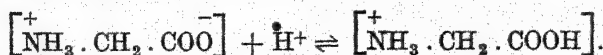


In the presence of an acid, the first type of ionisation will occur, the hydroxyl ions being removed by the added hydrogen ions. In the presence of an alkali, the second equation will express the ionisation, for the added hydroxyl ions will combine with hydrogen ions, and will tend to repress the formation of hydroxyl ions according to the first equation. Glycine forms both a hydrochloride and a sodium salt.

In the case of organic ampholytes, a third type of ion, which carries both a positive and a negative charge, can exist. These are known as "Zwitter" ¹ or "dual" ions. Thus, glycine can produce the Zwitter-ion $[\overset{+}{\text{NH}_3} \cdot \text{CH}_2 \cdot \text{COO}^-]$.

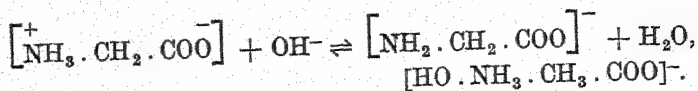


It is probable that in aqueous solution an amino-acid exists almost entirely in the form of the Zwitter-ion. The addition of an acid converts the Zwitter-ion into the basic ion $[\overset{+}{\text{NH}_3} \cdot \text{CH}_2 \cdot \text{COOH}]$,



The removal of the Zwitter-ion results in further dissociation, and the acid further dissolves. The addition of a base converts the Zwitter-ion into the acidic ion $[\text{NH}_2 \cdot \text{CH}_2 \cdot \text{COO}^-]$,

¹ German "Zwitter" = hybrid.

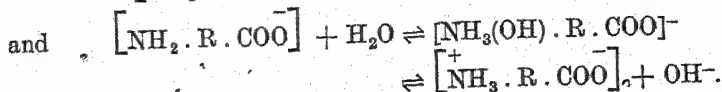
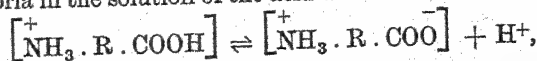


This can be compared with the action of acids and bases on ammonium acetate. If a strong acid is added to ammonium acetate, acetic acid is produced, together with ammonium ions; if a base is added, acetate ions and ammonia molecules are formed. In an amino-acid, of formula

$\text{NH}_2 \cdot \text{R} \cdot \text{COOH}$, the ions are thus $[\text{NH}_3^+ \cdot \text{R} \cdot \text{COOH}]$ and

$[\text{NH}_2 \cdot \text{R} \cdot \text{COO}^-]$, together with the Zwitter-ion $[\text{NH}_3^+ \cdot \text{R} \cdot \text{COO}^-]$.

The equilibria in the solution of the acid will be:—



Since the amino-acid is capable of removing both $[\text{H}^+]$ and $[\text{OH}^-]$ ions, it will make a good buffer (§ 330). The proteins consist of complex amino-acids, and there is little doubt that the constant p_{H} value of the protein-containing liquids of the body, such as the blood, is due to this buffer action.

334. Double Salts and Complex Salts.—When solutions of two different salts are mixed in equivalent proportions, and the mixture is evaporated, it sometimes happens that the crystals forming are composed of a double salt. Thus, if solutions of equivalent quantities of ferrous sulphate and of ammonium sulphate are mixed, and the solution is evaporated, there separates out as a crystalline phase, ferrous ammonium sulphate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. This salt is somewhat different in appearance and properties from the salts from which it was made.

If silver cyanide is added to potassium cyanide solution, it dissolves, and from the solution a new salt, potassium argento-cyanide, $\text{KAg}(\text{CN})_2$, is formed. This has notably different properties from either of the original salts. In solution there is no trace of silver ions detectable by chemical tests, but instead a complex ion, $(\text{Ag}(\text{CN})_2)^-$, exists, together with potassium ions. There are a very large number of salts such as this, which are called "complex salts".

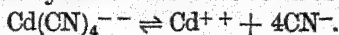
Examples of common complex salts are the ferro- and ferricyanides. The salts formed when silver chloride dissolves in ammonia, or in sodium thiosulphate, or in potassium cyanide, just mentioned, are complex salts.

There appears to be no definite line of demarcation between double salts and complex salts as far as chemical properties go. They are the extremes of a series of varying degrees of chemical combination.

The differences lie only in the degree of stability of the complex ion. In what are usually called double salts, the complex ion is readily broken down into its constituents. Some authors (e.g., Ephraim, *Inorganic Chemistry*, trans. P. C. L. Thorne) regard the schönites ($M^I SO_4 \cdot M_2^I SO_4 \cdot 6H_2O$), of which ferrous ammonium sulphate is one, as complex salts ($M_2^I [M^II (SO_4)_2]^{II} \cdot 6H_2O$). The alums likewise they take to be not $M_2^I SO_4 \cdot M_2^{III} (SO_4)_3 \cdot 24H_2O$, but $M^I [M^{III} (SO_4)_2] \cdot 12H_2O$. This view regards all the double salts merely as very unstable complex compounds. An $[M^{II} (SO_4)_2]^{--}$ ion probably exists in a solution of ferrous ammonium sulphate, and there would only have to be a small amount of dissociation into $M^+ +$ and $(SO_4)^{--}$ ions for these latter to be detected. As soon as they were removed from the solution by precipitation, more of the complex ion would decompose, giving, finally, complete breakdown of the complex ion.

Investigation of Complex Ions.—As a rule, complex salts are quite stable in the solid state, and X-ray analysis of their structure reveals the presence of the complex ion. There are, however, many ways in which the presence of complex ions in solution may be recognised. The chief of these are:—

(1) *Qualitative Analysis.*—It has already been stated that the complex salt ionises in a different way from a double salt. Although it contains two metals, one of them is to be found in the anion, and therefore is not evident in solution as a metal ion. Hence, the solution will not answer to the tests for that ion. Thus, if copper sulphate is treated with potassium cyanide a white precipitate of cuprous cyanide, $Cu_2(CN)_2$, is first produced, which dissolves in excess of the cyanide, giving a solution containing potassium cupro-cyanide, $K_2Cu(CN)_3$. This solution gives none of the tests for copper. Thus we find that if ammonium sulphide solution be added no black precipitate results. This fact is made use of in qualitative analysis in the separation of cadmium from copper. If to a solution containing both metals an excess of potassium cyanide is added, both metals form complex cyanides, but the cadmium compound is much less stable than the copper salt. Hence, addition of ammonium sulphide, or passage of hydrogen sulphide, precipitates the cadmium sulphide, but leaves the copper in the solution. The complex cadmium cyanide ion breaks down as follows:—



There is an equilibrium between these ions, and removal of Cd^{++} by ammonium sulphide results in the shifting of the equilibrium to the right, and so, finally, all the cadmium is precipitated. It is clear that only the most stable complex ions will fail to give the qualitative tests for their components.

The "transition" elements in the Periodic Table, together with the metals copper, silver and mercury, are all noted for the formation

of complex ions. The electronic theory provides an explanation of this.

(2) *Solubility Method*.—If an inorganic substance is sparingly soluble in water, but very soluble in some aqueous solution, it is very likely that complex ion formation has taken place. The solubility is easily explained. Consider as before silver cyanide. This salt is very sparingly soluble in water. It may be supposed, however, to give a few silver and cyanide ions:—

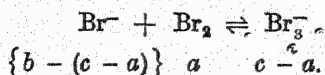


Addition of potassium cyanide should, on the theory of the solubility product (§ 335), depress the ionisation, and hence result in the precipitation of silver cyanide. What happens is, however, that the cyanide ion is removed as well as the silver ion in the formation of the complex $[\text{Ag}(\text{CN})_2]^-$, and hence the equilibrium is destroyed and the silver cyanide goes into solution. Actually, although so much silver cyanide dissolves, there is a decrease in the silver ion concentration.

(3) *Distribution Method*.—According to the Distribution Law, the equilibrium in two phases between which a substance distributes itself exists only between molecular species which are identical. This fact is frequently applied to the study of the equilibrium between the halides and the halogens. Thus, the solution of bromine in potassium bromide has been investigated by Roloff by this method. Solutions of potassium bromide were shaken with strong solutions of bromine in carbon disulphide. The bromine distributed itself between the bromide layer and the disulphide layer. The amount present in each was determined by volumetric analysis. The distribution of bromine between water and carbon disulphide was also found.

Suppose that on shaking water with a solution of bromine in carbon disulphide a gram-molecules of bromine pass into the aqueous layer per litre. When shaken with a solution of KBr containing b gram-molecules per litre, then c gram-molecules of bromine pass into the aqueous layer. Then $c - a$ gram-molecules of bromine must have been used up in forming complex ions.

Suppose that the equilibrium is represented by



If the concentrations are as indicated in italics above, by the Law of Mass Action

$$K = \frac{(b - c + a)a}{c - a}$$

Actually, Roloff found that K came out to be constant within the limits of experimental error, and so the above equation may be regarded as the correct one for expressing this equilibrium.

(4) *Ionic Migration Method*.—It is clear that the size of the ion and its nature will influence transport experiments (§ 306). Hence, in a transport experiment it would be possible to indicate the presence of complex ions, and this was done by Hittorf for potassium ferrocyanide. His results are interesting, and should be read in connection with this work in the chapter on Electrolysis (§ 307).

13.7207 Gms. of solution before electrolysis gave, when evaporated with sulphuric acid and ignited, 2.0505 gms. of potassium sulphate, and 0.4869 gm. of ferric oxide. After electrolysis 23.3087 gms. of solution from the anode compartment gave 3.2445 gms. of potassium sulphate, and 0.8586 gm. of ferric oxide. The amount of current flowing was shown by a silver voltameter. During the experiment 0.5625 gm. of silver was deposited. The analysis quoted shows that the anode solution after electrolysis contained 1.4585 gms. of potassium and 0.60096 gm. of iron. In potassium ferrocyanide 1.4585 gms. of potassium is equivalent to 0.5281 gm. of iron. The excess of iron in the anode chamber is therefore 0.07286 gm. = 0.002602 equivalent. The silver deposited is 0.00521 equivalent. Hence, the valency of an ion containing one equivalent of iron is $0.00521/0.002602$, or the valency of the complex ion containing 1 atom of iron is twice this, i.e., 4.

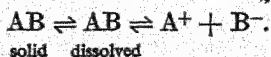
(5) *Electromotive Force Measurements*.—The use of this method is described in § 340.

(6) *Conductivity*.—This method was used largely by Werner in his study of co-ordination compounds.

The formation of complex compounds alters the number of ions present. Thus chromic chloride, CrCl_3 , should give four ions, but actually it gives only two, owing to the formation of the co-ordination compound $[\text{Cr}(\text{H}_2\text{O})_2\text{Cl}_2]\text{Cl}$. The conductivity is, therefore, proportionately diminished. The size of the ion also alters its mobility and therefore affects the conductivity of the solution.

(7) *Determination of Molecular Weight*.—It is known that the molecular weight of a substance in solution, as determined by any of the colligative property methods, is dependent upon the number of individual particles present. Thus, when hydrogen iodide is added to iodine solution, it is found that the freezing point of the latter is unchanged. Hence, there cannot have been any alteration in the number of individuals in the solution. In this way the number of possible complexes is limited.

335. Solubility Product.—If a solution of an electrolyte is in contact with the solid electrolyte, there are two simultaneous equilibria. The solid is in equilibrium with its solution, and the non-ionised electrolyte in equilibrium with its ions. Thus



If the Law of Mass Action holds

$$\frac{[A^+][B^-]}{[AB]} = K.$$

But, if there is solid present, the concentration of the undissociated electrolyte is constant, since the undissociated electrolyte is in equilibrium with the solid, which has a constant active mass. Hence, the product of the ionic concentrations will be constant, and

$$[A^+][B^-] = S.$$

This product is called *the solubility product*.

Note that we can only speak of a solubility product when there is excess of solid electrolyte remaining over. The solubility product is not the ionic product under all conditions, but only when there is excess of solid present, *i.e.*, when we are dealing with a saturated solution.

336. Applications of the Concept of Solubility Product.—The effect of an acid in dissolving a sparingly soluble salt was formerly regarded as the turning out of a weaker acid by a stronger one. But, according to the ionic hypothesis, the hydrogen ions furnished by the stronger acid combine with the anions of the salt, forming the more or less undissociated weaker acid, thus reducing the number of anions. Hence, the solubility product of the sparingly soluble salt is not reached, and it goes into solution. Thus calcium oxalate dissolves in dilute hydrochloric acid. If the salt is represented by CaOx , the solubility product is given by $[\text{Ca}^{+}] [\text{Ox}^{-}] = S$. If dilute hydrochloric acid is added, the hydrogen ions provided by the acid combine with the oxalate ions to give the little ionised oxalic acid. Thus the concentration of oxalate ions is reduced, and the product $[\text{Ca}^{+}] [\text{Ox}^{-}]$ is now less than S . Hence, the salt dissolves until the ionic product is again equal to S .

If, on the other hand, a solution of calcium oxalate in water is taken, and a solution of oxalic acid, containing a sufficient concentration of oxalate ions, is added, calcium oxalate will be precipitated, since the product $[\text{Ca}^{+}] [\text{Ox}^{-}] = S$ will have been exceeded. Similarly, if a solution of calcium chloride is added, precipitation may occur.

Summing up, for a substance AB , for which the solubility product is S , the solid salt can exist in equilibrium with its solution when

$$[A^+][B^-] = S;$$

when

$$[A^+][B^-] < S,$$

the salt dissolves; and when

$$[A^+][B^-] > S,$$

the solution is supersaturated, and salt deposits.

The solubility of the sulphides¹ in acids is governed by similar

¹ It is only possible to give a simplified account here. For a fuller discussion of the question see A. J. Mee, "The Precipitation of Sulphides", *School Science Review*, June, 1937.

relationships. The solubility products of some of the metallic sulphides are given in the following Table.

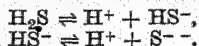
TABLE XCI.—SOLUBILITY PRODUCTS OF SULPHIDES

Sulphide	Solubility Product.	Sulphide.	Solubility Product.
MnS (buff) . . .	7×10^{-6}	NiS . . .	10^{-27}
FeS . . .	$\sim 10^{-20}$	PbS . . .	4×10^{-28}
MnS (green) . . .	6×10^{-22}	CdS . . .	$\sim 10^{-28}$
Tl ₂ S . . .	5×10^{-24}	CuS . . .	3×10^{-42}
ZnS . . .	10^{-24}	Hg ₂ S . . .	10^{-47}
CoS . . .	2×10^{-27}	Ag ₂ S . . .	10^{-50}
		HgS . . .	3×10^{-54}

Zinc sulphide dissolves in dilute hydrochloric acid, but only slightly in dilute acetic acid, whilst manganous sulphide dissolves readily even in dilute acetic acid. This can be explained as follows. The manganous sulphide has a solubility product of 7×10^{-6} . When dilute acetic acid is added, quite a small concentration of hydrogen ions is added, but these combine with sulphide ions to give the very little ionised hydrogen sulphide. Since the number of sulphide ions present is comparatively large (compared with other sulphides which dissolve only slightly in water), the product of hydrogen and sulphide ion concentrations is sufficient to exceed the solubility product of sulphuretted hydrogen,¹ and so the compound is produced. It may remain in solution, or may be partly given off as gas. In any case, sulphide ions are progressively removed from the solution, and all the manganous sulphide dissolves.

The solubility product of zinc sulphide is 10^{-24} . Here the solubility product is much smaller than that of manganous sulphide. The addition of dilute acetic acid is insufficient to provide hydrogen ions in great enough concentration to reach the solubility product of hydrogen sulphide when there are so few sulphide ions, and so the sulphide does not dissolve in dilute acetic acid. A little of it will dissolve, but an equilibrium will rapidly be reached. Dilute hydrochloric acid, however, contains sufficient hydrogen ions to cause the solubility product of

¹ Strictly speaking, hydrogen sulphide has not a solubility product in the sense of the definition given above. It is a weak dibasic acid which ionises in two stages:—



The dissociation constants are (§ 279):—

$$\frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 10^{-7}; \quad \frac{[\text{H}^+][\text{S}^{--}]}{[\text{HS}^-]} = 10^{-15}.$$

Hence,
$$\frac{[\text{H}^+]^2 [\text{S}^{--}]}{[\text{H}_2\text{S}]} = 10^{-22}.$$

In a saturated solution of the gas at 25° C. (to which temperature the above figures refer) $[\text{H}_2\text{S}] = 0.1$, and hence $[\text{H}^+]^2 [\text{S}^{--}] = 10^{-23}$. This may be regarded as the solubility product of hydrogen sulphide.

sulphuretted hydrogen to be reached, and hence the undissociated substance is formed and the sulphide dissolves.

Mercuric sulphide, with a solubility product of 3×10^{-54} , cannot provide enough sulphide ions to exceed the solubility product of hydrogen sulphide, even if a very strong acid is used. Hence, it is insoluble in all acids.

The precipitation of sulphides is governed by similar considerations. It is known that the sulphide ion concentration in an $M/5$ solution of hydrochloric acid, saturated with hydrogen sulphide, is about 10^{-22} . For precipitation to occur, the solubility product of the sulphide must be exceeded. Suppose the solutions of the metallic salts used are approximately $M/10$; then the concentration of metal ion in the solution must be about 0.1 when each molecule of salt gives one metal ion. Hence, the product $[\text{Metal}][\text{S}^{2-}]$ in such a solution of a metallic salt in hydrochloric acid, saturated with hydrogen sulphide, is $10^{-22} \times 0.1 = 10^{-23}$. Those metals with sulphides of solubility product less than 10^{-23} will be precipitated. Thus, cupric sulphide has the solubility product 3×10^{-42} . This value is more than reached if a 0.1 M solution of cupric chloride in 0.2 M hydrochloric acid is treated with hydrogen sulphide. Indeed, the value of the product is then 10^{-23} . Hence, cupric sulphide is precipitated. Certain metals lie on the border line. Cadmium sulphide has a solubility product about 10^{-28} . If the conditions outlined above hold, the sulphide will be precipitated on passing hydrogen sulphide through a solution of cadmium chloride in $M/5$ hydrochloric acid. If, however, the hydrochloric acid used is stronger, the value of $[\text{S}^{2-}]$ in the solution is less (since $(\text{H}^+)^2 [\text{S}^{2-}]$ must be constant), and the solubility product may not now reach 10^{-28} , especially if the solution is weak in cadmium ions. Zinc sulphide has a solubility product of 10^{-24} . This is just on the border line. In aqueous solution, $[\text{H}^+]^2 [\text{S}^{2-}]$ is 10^{-23} , and it has been shown that $[\text{S}^{2-}]$ is 10^{-15} . If hydrogen sulphide is passed through an $M/10$ aqueous solution of zinc sulphate, the product $[\text{Zn}^{2+}][\text{S}^{2-}]$ would be 10^{-16} . This is greater than the solubility product of zinc sulphide, and hence zinc sulphide is precipitated. In $M/5$ hydrochloric acid $[\text{S}^{2-}]$ is 10^{-22} . If $M/100$ zinc chloride in $M/5$ hydrochloric acid were to be treated with hydrogen sulphide, the product $[\text{Zn}^{2+}][\text{S}^{2-}]$ would be 10^{-24} , and the sulphide would just be precipitated. In stronger acid solutions $[\text{S}^{2-}]$ is less than 10^{-22} ; and so in solutions of zinc chloride of concentration less than about $M/5$ no precipitation occurs. If some substance is present in the solution which can buffer it, e.g., acetate ions, the hydrogen ions of the hydrochloric acid are removed as undissociated acetic acid, and so the value of $[\text{S}^{2-}]$ will rise almost to that found in aqueous solution. Thus, in presence of sodium acetate, zinc sulphide is readily precipitated.

The concentration of sulphide ions in an $M/10$ ammonium sulphide solution is 2×10^{-6} . Nearly all sulphides have solubility products

considerably less than this, so they are precipitated, even from very dilute solutions, by this reagent.

The use of a mixture of ammonium chloride and ammonium hydroxide to precipitate aluminium, iron and chromium in qualitative analysis is explained in this way. The hydroxides of the metals of the ammonium sulphide and ammonium carbonate groups (and magnesium) would be precipitated by ammonium hydroxide, the solubility product $[M^+][OH^-]^2 - S$ being exceeded, owing to the hydroxyl ions being supplied by the ammonia. If, however, ammonium chloride is added to the ammonium hydroxide, its ionisation is considerably repressed, since the concentration of ammonium ions has been increased, and $[NH_4^+][OH^-]$ must remain constant. Thus, there is a great decrease in the concentration of hydroxyl ions in the solution, and the solubility products of the hydroxides of the metals of the above groups and magnesium are now not reached.

The validity of the theory of solubility product has sometimes been called in question. There seems no doubt that it holds accurately, or fairly accurately, for sparingly soluble salts, but that for saturated solutions of substances which are moderately, or easily, soluble in water, there are considerable deviations. It has been found, however, that the solubility product for a given substance is not always constant. This is probably due to the fact that ions added to the saturated solution of a salt AB may exert some electrostatic effect on the ions A and B, making the solubility product either greater or less. The solubility product is constant when activities are substituted for concentrations (§ 204).

SUGGESTIONS FOR FURTHER READING

- GLASSTONE, S. "The Electrochemistry of Solutions." (*Methuen*, 1937.)
MEE, A. J. "The Precipitation of Sulphides." *School Science Review*, June, 1937.
BELL, R. P. "Acids and Bases." (*Methuen*, 1952).
BRITTON, H. T. S. "Hydrogen Ions." (*Chapman and Hall*, 1942.)
LINGANE, J. J. "Electroanalytical Chemistry." (*Interscience*, 1953.)

CHAPTER XVI

ELECTROMOTIVE FORCE

337. The Voltaic Cell.—A voltaic cell is made up of two electrodes dipping into a solution. In a voltaic cell chemical energy is converted into electrical energy. The Daniell cell may be taken as an example (see Fig. 203). The working of the cell may be illustrated by considering each electrode in turn. At the zinc electrode there is a tendency for zinc ions Zn^{++} to go into solution; each ion leaves two electrons at the electrode. The process will continue until equilibrium is established between the electrode and the solution. At equilibrium there is a definite difference of potential between the electrode and the solution.

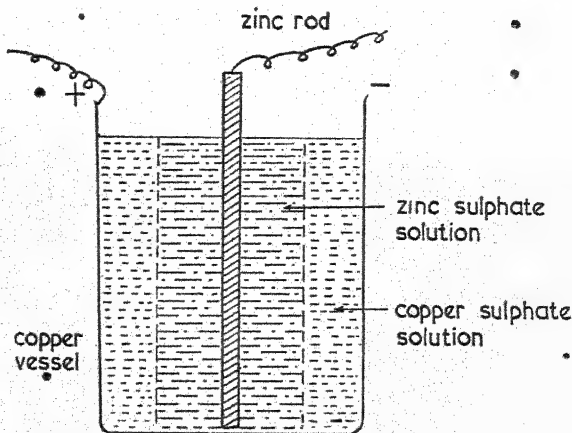


FIG. 203.—The Daniell Cell.

At the copper electrode the opposite process is taking place; copper ions Cu^{++} are depositing on the electrode giving it a positive charge. When the two electrodes are joined by a wire the excess electrons on the zinc electrode flow along the wire to neutralise the positive charge on the copper electrode. This flow of electrons constitutes the electric current. Conventionally the current is said to flow from the positive to the negative electrode; actually, as pointed out, the movement of electrons is in the opposite direction.

The electric current is produced because the reaction $\text{Cu}^{++} + \text{Zn} = \text{Cu} + \text{Zn}^{++}$ is taking place in the cell.

The flow of current in a cell depends upon a difference in potential between the two electrodes of the cell. The actual difference of potential between the two electrodes depends on the difference of potential between each electrode and the solution. Nernst calculated the potential of a single electrode by assuming that the tendency for ions to go into solution is dependent upon what he called the "solution pressure" of the metal forming the electrode. For a metal that tends to force ions into solution an excess of electrons is left on the electrode. The positive ions in solution collect around the electrons on the electrode forming an electrical double layer at the junction of the electrode and solution. The double layer will build up as more and more positive ions go into solution. Meanwhile, an opposite process involving the deposition of positive ions on the electrode will be taking place. This process is supposed to be related to the osmotic pressure of the ions in solution and will depend on the concentration of the ions. At equilibrium the two processes occur at the same rate. If the potential between the electrode and solution at equilibrium is E , then the electrical energy necessary to move one gram ion of metal ions back on to the electrode against potential E requires the expenditure of electrical energy $-nFE$ where n is the valency of the ions and F is equal to one Faraday. To take one gram ion from the metal at solution pressure P into solution against the osmotic pressure p requires energy $RT \log \frac{P}{p}$. (It will be noted that this equation is similar to that for the work done in the isothermal expansion of an ideal gas.) At equilibrium the energy of these two processes should be equal and hence:

$$-nFE = RT \log \frac{P}{p}$$

The osmotic pressure is proportional to the concentration of ion in solution so $-nFE = RT \log \frac{P}{kc}$ where k is a constant. Then

$$E = -\frac{RT}{nF} \log \frac{P}{k} + \frac{RT}{nF} \log c$$

The first term is a constant at any temperature for a particular metal and can be written E_o so

$$E = E_o + \frac{RT}{nF} \log c = E_o^{25} + \frac{0.059}{n} \log_{10} c;$$

In the last expression the temperature is assumed 25° C. and the logarithms have been converted to the base 10. E_o represents the potential between the electrode and the solution containing one gram ion of the metal. The Nernst expression is of the right form but the views on which it is based—particularly the idea of the solution pressure of a metal—are now considered obsolete.

It is only possible to measure a difference of potential between two

electrodes. A single electrode potential cannot be measured. For this reason E_0 for hydrogen is fixed as the zero of potential and all other potentials are measured relative to this. The hydrogen electrode in a solution of normal acid is at zero potential on this arbitrary scale. The Table XCII gives E_0 values on this scale for a number of metals.

TABLE XCII

Metal.	Ion.	Potential, volts.	Metal.	Ion.	Potential, volts.
Li	Li^+	- 2.96	Tl	Tl^+	- 0.33
Rb	Rb^+	- 2.92	Co	Co^{++}	- 0.29
K	K^+	- 2.92	Ni	Ni^{++}	- 0.23
Ba	Ba^{++}	- 2.80	Sn	Sn^{++}	- 0.14
Na	Na^+	- 2.71	Pb	Pb^{++}	- 0.12
Mg	Mg^{++}	- 1.55	Fe	Fe^{+++}	- 0.045
Al	Al^{+++}	- 1.28	H	H^+	0.00
Mn	Mn^{++}	- 1.10	Cu	Cu^{++}	+ 0.34
Zn	Zn^{++}	- 0.76	Hg	Hg_2^{++}	+ 0.80
Fe	Fe^{++}	- 0.44	Ag	Ag^+	+ 0.80
Cd	Cd^{++}	- 0.40	Au	Au^{++}	+ 1.36

This is the electronegative series of the metals. A metal having a negative potential has a greater tendency to go into solution as its ions than hydrogen has. It follows that if a metal having a certain potential is placed in a solution containing ions of a metal of a more positive potential, then the former will dissolve, and the ions of the metal in solution will be discharged and the element will be precipitated. Thus, if zinc is placed in a solution of copper sulphate, the zinc has a considerable negative potential, viz., - 0.76 volt, whilst copper has a positive potential of 0.34 volt. The zinc goes into solution, and the copper is precipitated, since the zinc has a greater tendency to dissolve as ions than the copper has. Lead will also precipitate copper from solution.

It is possible to determine the potential of certain non-metallic elements, but there are numerous difficulties. The following values have been obtained:—

TABLE XCIII

Element.	Ion.	Potential., v.
I	I^-	+ 0.54
O	OH^-	+ 0.40
Br	Br^-	+ 0.99
Cl	Cl^-	+ 1.36
F	F^-	+ 1.90

This matter has been dealt with in the simplest possible way. It should be realised that the equation from which the electrode potentials are calculated is not quite exact, and that the effect of pressure has been neglected. There are numerous refinements which cannot be discussed here.

If the standard electrode potentials of the elements are plotted against their atomic numbers, it is found that the electrode potential is a fundamental property of the element. There is quite a definite periodicity governed by the grouping of the periodic table. It is clear that this should be so, for the tendency of a substance to form ions depends upon the ease with which one electron or more can be lost from the electron shells round the nucleus. This will vary with the number present in the outer shell.

The electrode potential of a metal is *one* of the factors that decides whether it will dissolve in a dilute acid with evolution of hydrogen. The elements with negative potentials dissolve in dilute acids the more readily the greater the numerical value of the potential. It is not to be expected that copper will dissolve in dilute sulphuric acid, since the tendency for copper ions to go into solution is less than that for hydrogen ions to come out of it (the metal has a positive electrode potential). It must however be remembered that the strength of the acid may modify the electrode potential, that the above remarks refer only to normal solutions, and that there are other factors which must be taken into account if the question is to be studied fully.

It was originally thought that the electrical energy given by the cell as a result of the cell reaction is equal to the heat of the reaction. This is not so. Actually the electrical energy produced is equal to the change in Gibbs free energy brought about by the reaction, i.e.,

$$-\Delta G = nFE. \quad \text{But } \Delta G = \Delta H + T \frac{\partial(\Delta G)}{\partial T}. \quad \text{So}$$

$$nFE = -\Delta H + nFT \frac{dE}{dT}.$$

Whether the electrical work done is greater or less than the heat of the reaction depends on the temperature coefficient of the cell, that is the

variation of E with T . If $\frac{dE}{dT}$ is negative then $\Delta G > \Delta H$ and heat is

absorbed from the surroundings during the working of the cell. If $\frac{dE}{dT}$

is positive then $\Delta H > \Delta G$ and heat is given out to the surroundings of the cell in its working. The equations given above may be applied to measure the free energy change of the cell reaction.

338. Concentration Cells.—A particular case of a voltaic cell is one

in which two electrodes of the same metal are dipping into solutions of ions of the metal. The two electrode solutions are separate and in each electrode compartment the ions are at a different concentration. These are denoted by c_1 and c_2 (see Fig. 204). The difference in

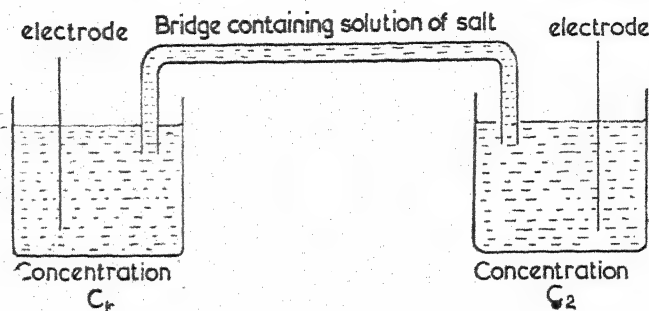


FIG. 204.—Concentration Cell.

potential between the two electrodes is $E_1 - E_2$ where E_1 is the difference in potential between the metal and the ions in compartment 1 and E_2 is similarly defined. Then

$$E_1 = E_o + \frac{RT}{nF} \log_e c_1$$

where E_o is the standard potential for the metal and n is the valency of the metal ions. Similarly:

$$E_2 = E_o + \frac{RT}{nF} \log_e c_2$$

$$\begin{aligned} \text{Thus } E_1 - E_2 &= E_o + \frac{RT}{nF} \log_e c_1 - E_o + \frac{RT}{nF} \log_e c_2 \\ &= \frac{RT}{nF} \log_e \frac{c_1}{c_2} \end{aligned}$$

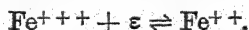
$$\text{At } 25^\circ \text{ C. and using common logarithms } E_1 - E_2 = \frac{0.059}{n} \log_{10} \frac{c_1}{c_2}$$

The electrode compartments are separated by a salt bridge and if the electrodes are connected by a wire a current will flow. As the current flows ions will deposit from the solution of greater concentration at the corresponding electrode and ions will go into solution in the compartment of lesser concentration. The process will continue until the concentrations of ions in the electrode compartments are equal. At this

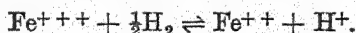
stage the difference in potential between the electrodes is zero. A cell of this type is known as a concentration cell. The working of a concentration cell depends on the tendency of a solute to distribute itself uniformly in a solvent. In the example above the cell only works until the concentrations in both compartments are equal.

339. Oxidation and Reduction Potentials.—In ionic processes, oxidation means an increase in the number of positive (or decrease in the number of negative) charges. Reduction is the reverse of this. In a mixed solution of ferrous and ferric ions, the solution will possess oxidising or reducing powers according as whether it can gain or lose electrons. Thus, if a platinum plate is dipped into such a solution, and the mixture tends to oxidise the plate, it will tend to remove electrons from the plate, thus giving it a positive charge; if it tends to reduce the plate, it will seek to give up electrons to the plate, giving it a negative charge. It is clear that the oxidising or reducing power of a solution may be measured by the magnitude and sign of the charge given to the platinum electrode. This charge gives rise to an electrode potential similar to those previously considered. If the platinum electrode in the solution is connected with a normal hydrogen electrode (§ 340) and the e.m.f. of the cell is measured, the value of the electrode potential may be obtained.

The solution will contain Fe^{++} , Fe^{+++} and H^+ ions. The last are, of course, necessary for the reaction to proceed. The reaction occurring is



This may be regarded as an oxidation of the Fe^{++} by hydrogen ion, which is thereby reduced to hydrogen gas. The equation may therefore be written



The equilibrium in the system is therefore governed by the equation

$$\frac{[\text{Fe}^{+++}](p_{\text{H}_2})^{\frac{1}{2}}}{[\text{Fe}^{++}][\text{H}^+]} = K' \quad (1)$$

where K' is the equilibrium constant, and p_{H_2} is the pressure of hydrogen gas. The platinum electrode may now be regarded as functioning as an ordinary hydrogen electrode, the potential of the electrode depending upon the hydrogen ion concentration and the pressure of the hydrogen gas. The potential will be given by

$$E = \frac{RT}{F} \log_e \frac{[\text{H}^+]}{(p_{\text{H}_2})^{\frac{1}{2}}}$$

Since, when $[\text{H}^+] = 1$, and $p_{\text{H}_2} = 1$, $E = 0$, by definition.

But, from (1) above,

$$\frac{[\text{H}^+]}{(p_{\text{H}_2})^{\frac{1}{2}}} = \frac{1}{K'} \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]}$$

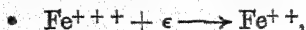
Hence,

$$E = \frac{RT}{F} \log_e \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]} + K,$$

where K is a constant. It has the dimensions of a potential, and may be called E_o , so that

$$E = E_o + \frac{RT}{F} \log_e \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]}.$$

Since, when $[\text{Fe}^{+++}] = [\text{Fe}^{++}] = 1$ (i.e., in a solution normal with respect to both ions) the logarithmic term is zero, it follows that E_o is the normal electrode potential of the process

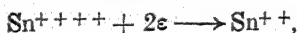


and is therefore called the "oxidation potential" of that process.

In the general case, where the difference between the valencies is n , the equation is

$$E = E_o + \frac{RT}{nF} \log_e \frac{c_2}{c_1}.$$

Thus, in the case of tin, the process is



and the equation governing it is

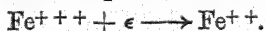
$$E = E_o + \frac{RT}{2F} \log \frac{c_2}{c_1}.$$

By measuring the voltages of cells made up, for example, as follows:—

Negative pole: Hydrogen electrode.

Positive pole: Platinum plate in a solution containing ferric and ferrous chlorides,

we can determine the oxidation potential of such reactions



The Table gives some of the values obtained for this and other similar reactions.

TABLE XCIV

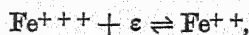
Reaction.	Potential, volts.
$\text{Co}^{+++} \longrightarrow \text{Co}^{++}$	+ 1.82
$\text{Pb}^{++++} \longrightarrow \text{Pb}^{++}$	+ 1.80
$\text{Ce}^{++++} \longrightarrow \text{Ce}^{+++}$	+ 1.57
$\text{Tl}^{+++} \longrightarrow \text{Tl}^{+}$	+ 1.24
$\text{Fe}^{+++} \longrightarrow \text{Fe}^{++}$	+ 0.76
$\text{Fe}(\text{CN})_6^{---} \longrightarrow \text{Fe}(\text{CN})_6^{--}$	+ 0.41
$\text{Cu}^{++} \longrightarrow \text{Cu}^{+}$	+ 0.17
$\text{Ti}^{+++} \longrightarrow \text{Ti}^{++}$	- 0.06
$\text{V}^{+++} \longrightarrow \text{V}^{++}$	- 0.2
$\text{Cr}^{+++} \longrightarrow \text{Cr}^{++}$	- 0.4

A positive sign means that a molar solution of the ions is more easily reduced than a molar solution of an acid is reduced to hydrogen.

What information can be gained from this table of oxidation-reduction potentials? Since the electrode $\text{Fe}^{++} \longrightarrow \text{Fe}^{+}$ has a positive potential of 0.76 volt compared with the hydrogen electrode, it follows that it is capable of accepting electrons more easily than will the hydrogen of an acid. Hence, the solution of ferric salt may be reduced by hydrogen under atmospheric pressure. The electrode $\text{Cr}^{++} \longrightarrow \text{Cr}^{+}$ possesses a negative potential of 0.4 volt. Hydrogen under atmospheric pressure cannot bring about this reduction, since a molar solution of Cr^{++} ions is less easily reduced to Cr^{+} ions than a molar solution of H^{+} ions is reduced to H . In fact, when a chromous salt is oxidised by hydrogen ions to a chromic salt, hydrogen is evolved. Hydrogen is also liberated from aqueous solutions of vanadous salts, and of the bivalent compounds of tungsten and samarium, oxidation taking place.

The reducing or oxidising powers of metals in contact with certain ions can also be obtained by considering the electronegative series of the metals, and the list of oxidation reduction potentials together. Thus, copper with an electrode potential + 0.34 volt can reduce ferric salts, though with greater difficulty than hydrogen. Silver, however, with an electrode potential + 0.80 volt, being more positive than the $\text{Fe}^{++} \longrightarrow \text{Fe}^{+}$ electrode, cannot bring about the reduction. Indeed, the reverse change will take place. Ferrous sulphate solution reduces silver nitrate to metallic silver.

Another method of representing the oxidising or reducing tendency of a system has been proposed. This is the r_{H} value. When a substance is an oxidising agent it *tends* to take up hydrogen; if it is a reducing agent it *tends* to evolve hydrogen. All oxidising and reducing actions are certainly not associated with the taking up or liberation of hydrogen, but they may, in effect, be regarded as such. The more a system tends to take up hydrogen, the greater is its oxidising power; the more it tends to evolve hydrogen, the greater is its reducing power. It follows that in a reversible oxidation-reduction system, such as

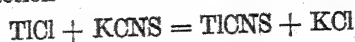


the pressure of hydrogen with which the system is *theoretically* in equilibrium (the p_{H_2} of equation (1), above), is a measure of the reducing or oxidising power of the system. In very few cases can this hydrogen pressure be actually measured, as it is so small, but it may be calculated from electrochemical observations. The r_{H} value for any system is the logarithm to the base 10 of the reciprocal of this hydrogen pressure, measured in atmospheres. By comparing r_{H} values, it is possible to say whether one system will oxidise another or reduce it.

340. Applications of Electrochemistry.—(a) *To the Study of Chemical*

Affinity or Change in Free Energy in a Reaction.—This has already been referred to in previous sections (§§ 112 and 337). The reversible e.m.f. of a cell is a measure of the free energy of the reaction going on in it. The validity of this method of determining affinity has been carefully tested by a number of observers, and particularly by Knüpfner and Bredig.

The chemical reaction



was carried out in a cell by means of the following arrangement.

Tl amalgam	KCNS solution saturated with TlCNS	KCl solution saturated with TlCl	Tl amalgam
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The e.m.f. of the cell was determined at various temperatures, and the free energy change calculated. If the electromotive force is a correct measure of free energy change, then the equilibrium constants calculated from the van't-Hoff isotherm should agree with those obtained by analytical methods. It is seen from the results given below that this is the case.

This provides strong evidence for the validity of the electrochemical method of determining free energy change.

The equilibrium constant, K , in the van't Hoff isotherm,

$$-\Delta G = RT \log K - RT \sum n \log C$$

is a function of the temperature, so that it is possible, by varying the temperature, to make the second term of the equation equal to the first, when the free energy change would be zero. At this temperature the electromotive force of the cell should be zero, if the free energy change is measured by this quantity. Knüpfner found that for the above cell

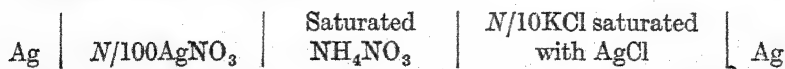
Temp.	K.	
	Calc.	Obs. (analytical).
39.9° C.	0.88	0.85
20° C.	1.26	1.24
0.8° C.	1.79	1.74

the e.m.f. was zero at 42.3° C. This was the value found experimentally by altering the temperature of the cell until it gave no e.m.f. The temperature calculated from the isotherm was 41.2° C., again in good agreement.

There seems little doubt then that the electromotive force method does indeed give a correct result for the free energy change of a chemical reaction.

(b) *To the Determination of the Solubility of a Sparingly Soluble Salt, and of Solubility Products.*—It is clear that the electromotive force of a concentration cell can be used to give the concentration of ions in a solution. For sparingly soluble substances the ionic concentration may be taken as the true solubility, the substance being supposed to be entirely dissociated. In this way the solubility of a sparingly soluble salt, such as silver chloride, can be determined with great accuracy.

Suppose that the following cell is set up:—



This cell is a concentration cell; it involves silver electrodes dipping into solutions of silver ions. The current flows through the cell from the potassium chloride side to the silver nitrate side. The potassium chloride is added in order to make the cell conduct. The silver chloride itself furnishes so few ions that the cell would have a very high resistance if this were not done. The saturated ammonium nitrate solution which forms the bridge between the two silver solutions is used to make the e.m.f. between the two silver solutions negligible. If this were not used, a correction would have to be applied to eliminate the effect of the junction potential. In the $N/10$ potassium chloride + silver chloride solution, the silver chloride gives rise to both silver and chlorine ions, but the concentration of chlorine ions from the silver chloride is negligible when compared with that from the potassium chloride. Hence, assuming that the potassium chloride is completely dissociated, the concentration of chlorine ions is 0.1.

If S is the solubility product, then

$$S = [\text{Ag}^+][\text{Cl}^-] \quad (1)$$

The solubility, M , $= \sqrt{S} = \sqrt{[\text{Ag}^+][\text{Cl}^-]}$

But $[\text{Cl}^-] = 0.1$, so that $M = \sqrt{[\text{Ag}^+] 0.1}$ (2)

The value of $[\text{Ag}^+]$ can be determined from the e.m.f. of the cell. If the e.m.f. is E , we have

$$E = \frac{RT}{nF} \log_e \frac{0.01}{c},$$

where c is the concentration in gram-equivalents per litre of Ag^+ ions required. Substituting for R , T , n , F , and bringing to common logarithms, the equation becomes

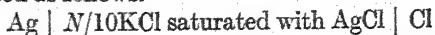
$$E = 0.058 \log_{10} \frac{0.01}{c},$$

where E is the e.m.f. in volts.

From this c can be calculated and substituted in equation (1), from which the solubility product can be obtained. The solubility can then be calculated.

A cell of a slightly different type has been used by Goodwin for the

determination of the solubility of silver chloride. This cell involves the use of a chlorine electrode (*i.e.*, a platinum foil, surrounded by chlorine), and is represented as follows:—



Since the chlorine electrode produces anions, the e.m.f. of the cell is not the difference between the two electrode potentials, but the sum of them. Thus we have for the e.m.f.

$$E = 0.058 \log \frac{[\text{Ag}^+]}{[\text{Ag}]} + 0.058 \log \frac{[\text{Cl}^-]}{[\text{Cl}]}$$

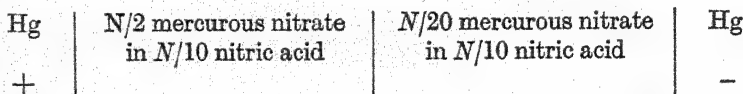
Now, $-0.058 \log [\text{Ag}]$ and $-0.058 \log [\text{Cl}]$ are merely the electrode potentials of Ag and Cl respectively, and are known. The e.m.f., E , is determined, and $[\text{Cl}^-]$ is known (0.1). Hence, $[\text{Ag}^+]$ can be calculated, and the solubility product obtained as before.

(c) *To the Determination of Valency.*—The expression for the e.m.f. of a concentration cell

$$E_1 - E_2 = \frac{RT}{nF} \log_e \frac{c_1}{c_2}$$

involves the valency of the ions, n . If, therefore, we know, or can determine, the values of the other quantities in the expression, n can be obtained.

The best example of the use of this method for finding valency is the work of Ogg on the valency of the mercurous ion. If the concentration cell



is set up, and its e.m.f. determined, n can be found by the following calculation. Let the concentration of mercury ions in the N/20 solution be c_1 , and that in the N/2 solution c_2 . If the liquid/liquid potential is neglected, we have

$$-E = \frac{RT}{nF} \log_e \frac{c_2}{c_1} = \frac{0.058}{n} \log_{10} \frac{c_2}{c_1},$$

where E is the e.m.f. of the cell. If it is supposed that the solutions are completely dissociated (which is, of course, only true to a first approximation), we have

$$\frac{c_2}{c_1} = \frac{20}{2} = 10.$$

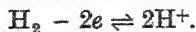
Ogg found the potential of the cell to be 0.029 volt. Hence,

$$0.029 = \frac{0.058}{n}, \quad \therefore n = 2.$$

Thus, the valency of the mercurous ion is 2, and it should be represented as Hg_2^{++} , the formula of a mercurous salt, say the nitrate, being $\text{Hg}_2(\text{NO}_3)_2$. There are many other pieces of evidence which point to

the same conclusion. The depression of the freezing point of dilute solutions of nitric acid when mercurous nitrate is dissolved in them provides evidence for the existence of Hg_2^{++} ions.

(d) *To the Determination of Hydrogen Ion Concentration.*—The electromotive force method is the most accurate for the determination of hydrogen ion concentration. Use is made of the hydrogen electrode, which consists of platinised platinum dipping into the solution of which the p_{H} is required, through which a current of hydrogen is passed. The platinum catalyses the electrochemical reaction



The electrode thus tends to become positively charged when hydrogen ions are converted into gaseous hydrogen, so that the electrode attains a definite potential when the electrostatic force repelling the hydrogen ions stops further discharge. The potential depends upon the concentration of hydrogen ions and the concentration of hydrogen gas.

The e.m.f. of a concentration cell is given by the relationship

$$E_1 - E_2 = \frac{0.059}{n} \log_{10} \frac{c_1}{c_2}.$$

It is obvious from this equation that if we know E_1 , E_2 , n , and c_2 we can find c_1 .

Hydrogen gas, in contact with a solution containing hydrogen ions, acts like a metal in contact with a solution containing ions of the metal. The potential of the hydrogen electrode in a solution normal with respect to hydrogen ions is taken as zero.

Suppose a cell is made up of two hydrogen electrodes one dipping in a solution of normal acid and the other dipping in a solution with an undetermined concentration of hydrogen ion say c_1 . In this cell $c_2 = 1$, $n = 1$, and E_2 is by definition zero, so we have $E_1 =$ the cell e.m.f. $= 0.059 \log c_1$. Thus a measurement of e.m.f. E_1 will enable us to determine c_1 the concentration of hydrogen ion and therefore the p_{H} of the solution.

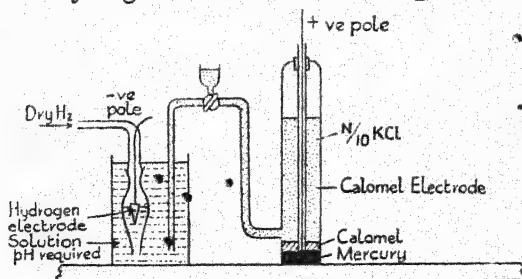


FIG. 205.—Arrangement of Cell for determining Hydrogen Ion Concentration.

Thus, if we had two hydrogen electrodes, one placed in a solution normal with respect to hydrogen ions and the other in a solution of which the hydrogen ion concentration was required, the two solutions

being separated by a porous partition or a bridge of some kind, by measuring the difference of potential we should find the hydrogen ion concentration by using the method above.

The hydrogen electrode used in practice may take one of many forms. The essentials are, however, shown in the left-hand electrode of Fig. 205. Hydrogen under a known pressure bubbles through a solution containing hydrogen ions, in which is immersed a strip of platinised platinum foil. Electrical connection is made with this foil.

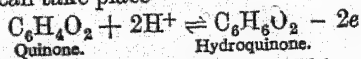
This electrode should be connected to a hydrogen electrode dipping into a normal solution of an acid—the normal hydrogen electrode. However, it is not always easy to get exact normality, and it is difficult to set up such an electrode, so the normal hydrogen electrode is usually replaced by a *calomel electrode*, which has a constant potential, known on the hydrogen scale. The calomel electrode is really a mercury electrode. It is made by placing a pool of mercury at the bottom of a vessel, and covering it with a paste of pure mercurous chloride, mercury and potassium chloride solution. The strength of the latter partly determines the e.m.f. of the electrode; hence, the strength must be specified. It is usual to employ $N/10$, N , or saturated solution. The cell is filled with potassium chloride solution of the correct strength, saturated with mercurous chloride.

A diagram of the two electrodes, arranged to determine the hydrogen ion concentration of a solution, is given above. The determination of the e.m.f. of the cell, by means of a potentiometer, calls for no description, as it is given in the practical text-books.

The e.m.f. of the calomel electrode referred to the normal hydrogen electrode is 0.3989 volts.

The quinhydrone electrode is another arrangement in use for determination of electrode potentials. It is not of such general use as the hydrogen electrode, since it can only be used for acid solutions in which the p_H is numerically less than 7, and is not reliable in the presence of certain neutral salts. It is, however, easier to set up than the hydrogen electrode, and does not require a continuous supply of hydrogen.

If quinone and its reduction product, hydroquinone, are present together in a solution which also contains hydrogen ions, the following reversible reaction can take place



provided that the electricity $2e$ is removed. This can readily be done by placing in the solution a piece of platinum foil and making the arrangement part of a cell. The potential of the electrode can be obtained by a method similar to the last. By direct comparison of a quinhydrone electrode against a hydrogen electrode, the expression

$$E = 0.704 + 0.058 \log_{10} [\text{H}^+]$$

was found by Büllmann to give the e.m.f. of the electrode at 18°C .

The Glass Electrode.—When a glass surface is in contact with a solution it acquires a potential, which depends upon the hydrogen ion concentration of the solution. This observation, which was made as far back as 1909 by Haber and Klemensiewicz, is now used as a basis of a method of determining the p_H of a solution where other electrodes cannot be used. The glass electrode consists essentially of a very thin-walled glass bulb, A, made of a low melting point glass, blown at the end of a glass tube. This is filled with an electrolyte, e.g., *N* hydrochloric acid saturated with quinhydrone. The upper end of the tube is ground, and a terminal, T, bearing a platinum wire, with which electrical contact is made with the electrolyte in the tube, is fitted over the ground portion. The bulb is then placed in the liquid B, of which the p_H is required and the potential is measured against a standard electrode C by means of a potentiometer. Since the resistance is high, a special galvanometer must be used. The potential of the electrode is connected with the p_H of the solution by the equation

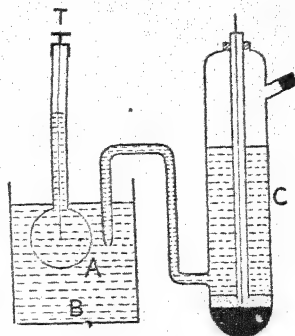


FIG. 206.—Glass Electrode.

$$E = K + \frac{RT}{F} \log_e [H^+].$$

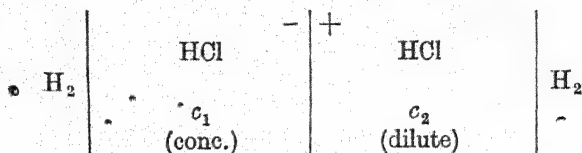
K is a constant for the electrode depending upon the nature of the glass and the electrolyte used in the bulb. It can be determined by finding the e.m.f. produced in buffer solutions of known p_H . If a curve is drawn between p_H and e.m.f., the p_H of any solution measured with the glass electrode can be read off directly when the e.m.f. produced is known.

The nature of the glass used is important. It must not be appreciably attacked by the liquid under test, and yet must have as high a conductivity as possible. The latter condition is fulfilled by soda-glass, but this is very easily attacked by alkali. For this reason, the results obtained by the glass electrode are not reliable for alkaline solutions of p_H greater than 10.

By the electromotive force method accurate determinations of p_H can be made, and if the apparatus is kept ready, as it can be, where the determination has frequently to be made, it is quite rapid. Under ordinary circumstances, however, it would be too slow, but commercial p_H meters based on the electromotive force methods have been developed. Accurate determinations of p_H can be made on these instruments very rapidly.

As pointed out in the last chapter, measurements of p_H can also be applied to determine the degree of hydrolysis of salts, so measurements of e.m.f. can also be used for this purpose.

(e) *To the Determination of Transport Numbers.*—We have not yet investigated the liquid/liquid potential in a cell. In the derivation of the formula (§ 324), it will be remembered, this potential was neglected, and then, in order to make this assumption correct practically, a bridge solution of ammonium nitrate was introduced into the cells. The reason for the liquid/liquid potential is that there is a transference of ions unequally, due to the differing mobilities of the ions. In the derivation of the formula (§ 324), it was assumed that when a Faraday of electricity passed through the cell, the effect would be to add one gram-ion to the anode compartment of the cell, and remove one gram-ion from the cathode compartment. This is not what happens, because the ions have different mobilities. Consider the cell



Suppose that c_1 is greater than c_2 . Then osmotic pressure tends to make the hydrochloric acid diffuse from the concentrated to the dilute solution. The hydrogen ion H^+ has a greater mobility than the chlorine ion Cl^- , and tends to outstrip it, giving rise to an e.m.f. at the junction such as to slow up the hydrogen ions, and hasten the chlorine ions, till both diffuse across at the same rate, as they must. Thus, the dilute solution (c_2) becomes positive relative to the concentrated solution (c_1). Let the liquid/liquid potential be $E_{\text{liq.}}$. When one Faraday of electricity passes through the cell, m_a gram-equivalents of Cl^- pass across the boundary in the one direction and m_c gram-equivalents of H^+ pass across in the other. The respective amounts of work done are:—

$$m_a F E_{\text{liq.}} = m_a R T \log_e \frac{c_2}{c_1},$$

and

$$m_c F E_{\text{liq.}} = m_c R T \log_e \frac{c_1}{c_2},$$

assuming that the acid is 100 per cent. ionised. In our case, $m_c > m_a$.

Adding, and remembering that $m_c + m_a = 1$, we have,

$$F E_{\text{liq.}} = (m_c - m_a) R T \log_e \frac{c_1}{c_2};$$

i.e.,

$$E_{\text{liq.}} = (m_c - m_a) \frac{R T}{F} \log_e \frac{c_1}{c_2},$$

directed from c_2 to c_1 .

Taking no account of the liquid/liquid potential, the e.m.f. of the concentration cell is given by

$$E = \frac{RT}{F} \log_e \frac{c_1}{c_2} = (m_c + m_a) \frac{RT}{F} \log_e \frac{c_1}{c_2},$$

directed from c_1 towards c_2 .

To obtain the total potential, E_T , we form the *algebraic* sum of E , and $E_{\text{liq.}}$, i.e.,

$$\begin{aligned} E_T &= \left[\frac{RT}{F} \log_e \frac{c_1}{c_2} \right] [m_c + m_a - (m_c - m_a)], \\ &= 2m_a \cdot \frac{RT}{F} \cdot \log_e \frac{c_1}{c_2}, \end{aligned}$$

directed from c_1 towards c_2 .

This equation involves the transport number of the anion, and can be made use of to determine this constant. A double cell (or "concentration cell without transport") is arranged as follows:—



If the hydrogen chloride is supposed to be completely dissociated, the e.m.f. of this cell, with the bridge solutions, is

$$E_1 = \frac{RT}{nF} \log_e \frac{c_1}{c_2},$$

since the two calomel electrodes exert an equal and opposite effect on the potential, and the system reduces to a hydrogen concentration cell without the liquid/liquid potential. If no bridge solutions are used, the different concentrations c_1 and c_2 of the acid affect the partial potentials at the hydrogen electrodes, and also the partial potentials of the calomel electrodes. These two effects are equal, and add together, giving for the e.m.f. of the cell *without bridge solutions*

$$E_1' = \frac{2RT}{nF} \log_e \frac{c_1}{c_2}.$$

The e.m.f. of a single hydrochloric acid concentration cell, consisting of two hydrogen electrodes dipping into acid of concentrations c_1 and c_2 (concentration cell with transport), would be

$$E_2 = \frac{2m_a RT}{nF} \log_e \frac{c_1}{c_2}.$$

If E_1 (or E_1') and E_2 are measured, it is clear that m_a can be calculated. The transport number of the cation, m_c , is equal to $1 - m_a$. This method yields results which are in excellent agreement with those determined by the usual Hittorf apparatus.

(f) *To the Study of Allotropy.*—If an element exists in two forms, there will be a potential difference between them when placed in a solution containing ions of the element. Thus, tin exists in two forms, white and grey. The change from the one to the other is a very slow process at ordinary temperatures. In order to determine the transition point, Cohen prepared a cell with ammonium stannichloride, $(\text{NH}_4)_2\text{SnCl}_6$, as electrolyte, and white and grey tin as the electrodes. The temperature of the cell was then altered, and it was found that at 18°C . the cell gave no e.m.f. This temperature must be that at which the two forms are equally stable, i.e., the transition temperature.

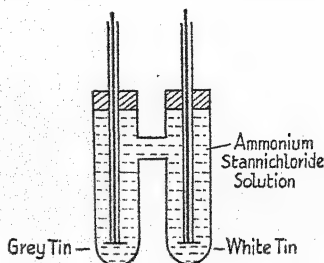


FIG. 207.
Cell for studying Allotropy of Tin.

A similar method can be used for determining the transition points of salt hydrates. Thus, to determine the transition point of the change of zinc sulphate heptahydrate into zinc sulphate hexahydrate a cell is prepared as shown in Fig. 208. The limb A contains a saturated solution of the heptahydrate and some of the solid salt. B contains a saturated solution of the hexahydrate together with some of the salt. The tube C, which links the two, is bent downwards to prevent the mixing of the solutions by convection currents. Two zinc electrodes go to the bottoms of tubes A and B. The cell is placed in a thermostat and connected with a galvanometer. At temperatures below the transition point the solubility of the hexahydrate, which is the metastable form, will be greater than that of the heptahydrate (§ 144). Hence, a current will flow outside the cell, from the electrode in the hexahydrate solution to that in the heptahydrate. At the transition point the solubilities become

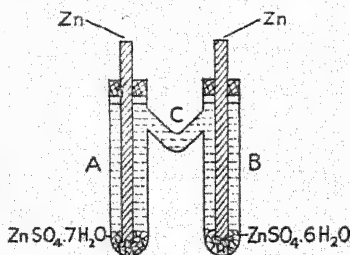


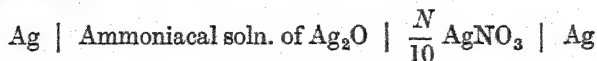
FIG. 208.—Cell for determining Transition Point of Hydrate of Zinc Sulphate.

equal and the cell then gives no e.m.f. At temperatures slightly above the transition point the direction of flow of the current is reversed. By noting the temperature at which the cell gives no e.m.f., i.e., when there is no deflection of the galvanometer on completing the circuit, the transition point is obtained to a high degree of accuracy.

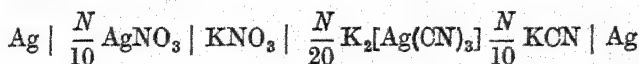
In the example given, the electrodes consisted of the same metal as the ions in the solution, but in some cases this cannot be arranged, and, in fact, it is not always necessary. For example, to determine the transition point of sodium sulphate

decahydrate, it is convenient to use a suitable non-polarisable mercury electrode.

(g) *To the Study of Complex Ions.*—By means of a concentration cell it is possible to determine the concentration of ions in a solution of a complex salt. For example, the concentration of silver ions in a solution of a complex silver salt, say diamminoargentic nitrate, can be found by preparing the cell



and determining its e.m.f. In this way the degree of dissociation of the complex ion and its instability constant can be found. The stability of the complex $[\text{Ag}(\text{CN})_3]^-$ can be found by determining the e.m.f. of the cell



The instability constant k is $\frac{[\text{Ag}^+][\text{CN}^-]^3}{[\text{Ag}(\text{CN})_3]^-}$

and can be found from the data arrived at experimentally.

There is little difference between a complex salt like potassium ferrocyanide and a double salt like ferrous ammonium sulphate. The classification of a salt into one or other of these classes can usually be made by considering its stability constant. Thus, potassium ferrocyanide gives rise to a complex ion, $[\text{Fe}(\text{CN})_6]^{4-}$, which is very stable, whilst ferrous ammonium sulphate gives rise to a complex ion, $[\text{Fe}(\text{SO}_4)_2]^{2-}$, which is very unstable. The e.m.f. method thus allows one to find the stability of the complex ion, and enables a classification to be made; even so, this is a matter of some difficulty, as ions are known of all stabilities from that of the ferrocyanide ion to that of the ferrosulphate ion, and it is difficult to draw the line between the two classes (§ 334).

(h) *Potentiometric Titrations.*—If reference is made to the curves drawn in §§ 330 and 331, representing the p_H changes which occur as a base is neutralised with an acid, it will be noted that there is a sudden change of p_H at the neutralisation point, and that this will be more marked the stronger the acid or base used in the titration. Thus, if a hydrogen electrode were to be immersed in the liquid there would be a sudden change in the e.m.f. at the points of inflexion in the curves. Obviously, if the e.m.f. is measured, and this can be done by means of a potentiometer, it is possible to find the end-point very accurately.

The method has several advantages over the ordinary indicator method. In the first place, the method can be used with coloured solutions where indicators would be useless, *eg.*, in the titration of vinegar. Secondly, it is possible to make the method automatic. When the

e.m.f. reaches a certain value, a relay is brought into operation which stops the liquid from running from the burette. Electrometric methods are now used extensively for the investigation of precipitation reactions as well as for neutralisation of an acid by a base.

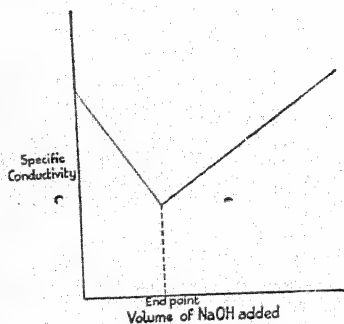


FIG. 200.—Curve for Conductometric Titration.

A similar type of titration is the conductivity titration which depends upon the fact that the conductivity of a solution is dependent upon the number of ions present and upon their mobility. Thus, when hydrochloric acid is neutralised by the addition of sodium hydroxide, the solution contains first of all hydrogen ions and chlorine ions. Since the hydrogen ion possesses the greatest mobility of any ion, it follows that the greater part of the conductivity will be due

to it. As sodium hydroxide is added, sodium ions are introduced, but hydrogen ions are removed, and the solution at neutralisation contains only sodium and chlorine ions, and will have a considerably smaller conductivity than the original acid. Now, if a little sodium hydroxide is added after the neutralisation, there will be a small concentration of hydroxyl ions, and the conductivity will at once rise, since the hydroxyl ion has the second greatest mobility. Thus, if the conductivity is plotted against the quantity of sodium hydroxide added, a curve is obtained with a sudden break in it. The break occurs at the neutralisation point.

The method has the advantages that it can be used with coloured solutions and will work where no indicator is found to be satisfactory. However, it is necessary to keep the temperature constant, and to have one of the constituents (that which is added) fairly concentrated, to avoid diluting the solution.

(i) *Determination of Degree of Displacement of One Metal from Solution by another.* As an example of this consider the Daniell cell. The reaction will continue until there is no potential difference between the electrodes: hence at this point $E_{Zn} = E_{Cu}$ and

$$E_{Zn}^{Zn} + \frac{RT}{nF} \log_e [Zn^{++}] = E_{Cu}^{Cu} + \frac{RT}{nF} \log_e [Cu^{++}]$$

Substituting for $\frac{RT}{E}$, n , E_{Cu}^{Cu} , E_{Zn}^{Zn} and converting to common logarithms

$$\text{gives: } -0.76 + \frac{0.059}{2} \log_{10} [Zn^{++}] = 0.34 + \frac{0.059}{2} \log_{10} [Cu^{++}]$$

$$-0.295 (\log_{10} [Zn^{++}] - \log_{10} [Cu^{++}]) = 1.10$$

$$\log_{10} \frac{[\text{Zn}^{+}]}{[\text{Cu}^{+}]} = 37$$

$$\text{or } \frac{[\text{Zn}^{+}]}{[\text{Cu}^{+}]} = 10^{37}$$

At equilibrium, when the copper and zinc potentials are equal, the ratio of the concentration of zinc to that of copper is about 10^{37} . In other words copper is almost completely displaced from solution by zinc.

341. Polarisation.—When a voltaic cell, consisting of a zinc and a copper plate in dilute sulphuric acid, is set up and a current is taken from it, the e.m.f. of the cell rapidly falls. This is because the electrodes become covered with bubbles of gas, which make gas electrodes with e.m.f.'s opposite to that of the cell. If the bubbles of gas are removed, mechanically or chemically, the e.m.f. of the cell remains constant. This phenomenon of a reverse e.m.f. brought about by the presence of the products of electrolysis is called *polarisation*. For a given concentration of electrolyte, the polarisation e.m.f. for any given type of cell is constant. Of course, exactly the same phenomenon is met with in electrolysis, in which the reactions are just the reverse of those taking place in a cell. Thus, if dilute sulphuric acid is electrolysed between platinum electrodes, a certain minimum e.m.f. must be applied to the electrodes to bring about continuous electrolysis. At first, a very small e.m.f. will bring about electrolysis, but almost immediately the electrodes become coated with bubbles of gas which exert an opposing effect, and, unless the applied e.m.f. is greater than the polarisation e.m.f., electrolysis almost stops. A slight current flows when the electrolysing e.m.f. is less than the opposing polarisation e.m.f., owing to diffusion of the gases away from the electrodes.

This polarisation may also be brought about by changes in concentration of the electrolyte. If a solution of copper sulphate is electrolysed between copper electrodes, at first a very small e.m.f. will suffice to cause electrolysis; but, after a while, the concentration of copper sulphate in the neighbourhood of the anode and cathode respectively, alters, owing to the different transport numbers of the copper and sulphate ions. Thus a concentration cell is set up, the e.m.f. of which opposes the electrolysing e.m.f.

The minimum voltage required for appreciable electrolysis is called the *decomposition potential*. This will vary from metal to metal. The value of the decomposition potential clearly depends on the electrode potential of the electrode in contact with the solution of its salt. This fact is made use of in depositing metals from solutions in which they are mixed. Thus copper and zinc may be separated electrolytically. The decomposition potential of copper sulphate is 1.49 volts, and of zinc sulphate 2.55 volts, using electrodes of copper and of zinc respectively. If copper plates are used as electrodes in the electrolysis of this solution,

copper only will be deposited if the electrolysing potential is less than about 2.5 volts.

In electrolysis the current is carried by the movement of all ions to the electrode. The discharge of ions takes place in order of decreasing reduction potential. Most ions are discharged at their reversible potential.

342. Hydrogen Overvoltage.—Theoretically, since the electrode potential of lead is -0.12 volt, when an acid solution of a lead salt is electrolysed between lead electrodes, hydrogen should be liberated at the cathode, and no lead. Actually, however, lead is deposited (cf. the lead accumulator). This is because most metallic electrodes have to be raised to a higher potential than that indicated in the electronegative series in order to enable hydrogen to be liberated. This additional voltage is known as *hydrogen overvoltage*. It varies from metal to metal.

The existence of overvoltage explains numerous phenomena. In the first place, it explains why the lead accumulator is a practical piece of apparatus. If it were not for the considerable overvoltage of this metal, lead would not be deposited on the negative plate when the cell was charged. If the lead is covered with a layer of a metal with a very low overvoltage, e.g., platinum, and the electrolysis is carried out, no lead is deposited, but hydrogen is liberated.

Overvoltage is made use of in many electrolytic processes. If electrodes with high overvoltages are used in electrolytic reductions it amounts to the same thing as enhancing the activity of the hydrogen. It is for this reason that lead electrodes are frequently used instead of platinum in some organic electrolytic reductions (e.g., the reduction of nitrobenzene).

If it were not for the existence of hydrogen overvoltage it would not be possible to deposit electrolytically metals which have a more negative potential than hydrogen (such as tin, zinc, and cadmium) from an acid solution. This can be done, if care is taken to ensure the absence of impurities which would deposit on the cathode and reduce its overvoltage.

It appears that the preferential liberation of ^1H compared with ^2H in the electrolysis of dilute sulphuric acid containing both ions is due largely to the greater overpotential of ^2H at a platinum electrode (§43).

Although a great deal of research has been carried out on overvoltage, no satisfactory explanation of the phenomenon has yet been offered.

Overvoltage occurs also at electrodes at which gases other than hydrogen are evolved.

343. The Polarograph.—Electrolysis can be applied to analysis by using an instrument called the polarograph. This instrument consists of an electrolytic cell with two mercury electrodes. One electrode consists of a pool of mercury at the bottom of the cell; the other is a

mercury drop at the end of a capillary tube. The mercury is dropping from the capillary tube and hence the surface of this electrode is being renewed constantly. When studying reduction phenomena the dropping electrode is the cathode; the still electrode the anode. The electrodes are reversed when studying oxidation reactions.

A common application of the polarograph is the study of the reduction reactions taking place with the discharge of metallic ions, for example, when a copper ion is discharged to form a copper atom. The ion is reduced because it gains electrons. If we have a mixture of metallic ions in solution and a gradually increasing potential is applied across the cell only a small current will flow through the cell. When the potential reaches the discharge potential of one of the ions in the solution the current flowing through will rise steeply and then level off. The rise is caused by the discharge of the ion which leads to the flow of current through the cell; the levelling off is due to concentration polarisation. The ions which are discharged first are those in the vicinity of the cathode. As these ions are discharged, they are replaced by ions diffusing into the cathode region from the main bulk of the solution. The diffusion is slow, and limits the rate of discharge after the ions originally present in the cathode region have been discharged. The result of this is that the rise in current is retarded and further current is limited by the diffusion; this is called the diffusion current. The speed at which concentration polarisation sets in and hence the height of the rise in current is dependent on the concentration of ions in the solution. Further the potential half-way up the rise, or—wave as it is called—is characteristic of a particular ion. (It is called the half-wave potential.) After one ion type in the solution has been discharged further ions will discharge as their decomposition potential is reached and thus the current-voltage curve of a solution containing a mixture of ions will show a number of such waves, each wave corresponding to the discharge of each type of ion. Observation of the half-wave potential and comparison with standard tables of half-wave potentials enables the ions present in the mixture to be identified. Further by using standard solutions of these ions and comparing the heights of the waves so obtained with those obtained in the mixture we can determine approximately the quantity of each ion present. Thus the polarograph provides a convenient method of qualitative and quantitative analysis of an unknown mixture.

SUGGESTIONS FOR FURTHER READING

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CHAPTER XVII

COLLOIDS AND SURFACE PHENOMENA

344. General.—An ordinary solution consists of a solvent and a solute. The particles of solute in ordinary solution are usually either normal molecules or ions. In a colloidal solution the particles of solute are much larger: they may consist of aggregates of hundreds of ordinary-sized molecules or even of a single large or macro-molecule. (Proteins are an example of substances with large molecules which form molecularly dispersed colloidal solutions.)

A colloidal solution cannot always be distinguished from a true solution with the naked eye. The particles, even though they may consist of some thousands of molecules, will pass through a filter paper, and cannot be seen under the microscope. A colloidal solution, however, is a two-phase system, whereas a true solution is regarded as being homogeneous, and therefore consists of only one phase.

Since the vast majority of substances have been obtained in colloidal solution, it is now customary to use the word "colloid" to represent a state of matter.

345. Historical Development of Colloid Chemistry.—Graham is usually regarded as the founder of the science of colloids. He certainly laid the foundation of the more serious study of the subject by his researches on liquid diffusion (1851–61), but many of the phenomena he noted and that have been noted since were well known very early in the history of chemistry.

Colloidal solutions of metals were fairly well known at Graham's time. The method of obtaining colloidal gold by reduction of gold salts with tin solutions was known as early as 1685. Berzelius was acquainted with a number of colloidal solutions. He refers to colloidal arsenious sulphide in the words: "For the present this solution is rather to be regarded as a suspension of transparent particles, for arsenious sulphide gradually separates out as a precipitate". He also knew of colloidal silica, which he obtained by the hydrolysis of silicon sulphide. " β -silicic acid is obtained in its purest form when silicon sulphide is oxidised by water; hydrogen sulphide is evolved as a gas, and the β -silicic acid dissolves in the water. In a more concentrated state the solution soon turns to a gelatinous mass." Sobrero and Selmi, in 1850, gave an elaborate account of the preparation of colloidal sulphur, though, of course, it was not known by that name.

The researches of Graham occupied a number of years, his first paper

on the subject appearing in 1851, whilst the last was published in 1861. Graham compared the rates of diffusion of a large number of substances, both inorganic and organic, and considered that liquid diffusion could be compared to volatility. He says, "the range in the degree of diffusive mobility exhibited by different substances appears to be as wide as the scale of vapour tensions". Certain substances, whilst varying among themselves in diffusibility, agree in diffusing much more rapidly than substances falling into another class, and they are therefore the "volatile" substances. These are salts and normal liquids. The other much more difficultly diffusible class comprises substances which are difficult to crystallise, such as starch, gum, tannin, albumen, gelatine, and glue. Graham called the first class *crystalloids* and the second *colloids*, from the Greek word *Kolla*, meaning "glue".

The difference between the classes was not very definite. Many substances appeared to be on the borderline. Nevertheless, the classification served a very useful purpose in chemistry.

346. General Nature of Colloids.—Crystalloids are capable of diffusing through a colloidal membrane, such as parchment, almost as quickly as they can diffuse through water, whilst colloids are remarkable in being unable to diffuse through such membranes. This fact was noted by Graham, who said that "of all the properties of liquid colloids, their slow diffusion in water, and their arrest by colloidal septa are the most serviceable in distinguishing them from crystalloids".

This property is made use of in dialysis, a process used in the purification of colloidal solutions and which will be further referred to later (§ 348).

Graham also noted that "solutions" of substances which were normally insoluble in water could be obtained, and that these behaved just like the colloids in many respects. They behaved similarly on dialysis, and often could be set to a jelly or coagulated by adding a salt. He used the term "sol" for a colloidal solution, and the word "gel" for the products of coagulation.

Ostwald regarded colloidal solutions as essentially heterogeneous systems, consisting of two phases, a disperse phase, which consisted of the colloidal particles, whilst the other was the dispersion medium. A colloidal solution of silver in water consisted of a disperse phase (the very finely divided silver), and the dispersion medium (water).

Colloidal solutions cannot be regarded as an entirely new section of the whole range of solution. Actually they are intermediate between solutions and precipitates, and there is a gradual transition between the two. Colloidal particles may be fairly large, bordering on being a precipitate, whilst they may be very small, bordering on true solution. It is usual to measure the diameter of colloidal particles in $m\mu$.¹ 1μ is

¹ The term $\mu\mu$ may sometimes be met instead of $m\mu$, but the latter is the form sanctioned by the Chemical Society.

10^{-4} cm., and $1\text{ }m\mu$ is 10^{-7} cm. Colloidal particles may be from 1 to $100\text{ }m\mu$ in diameter. Above the latter they are suspensions, and below the former they cannot be distinguished from true solutions.

The degree of dispersion, then, is the characteristic that marks out the colloid. Von Weimarn has shown that the degree of dispersion of a precipitate can be varied at will by correct choice of the concentrations of reacting solutions. In this way it is possible to make any precipitate into a colloidal solution. The relationship obtained by von Weimarn is

$$\delta = \frac{C}{S} \eta$$

δ being the fineness of the particles (smaller the larger the particles), S the solubility of the slightly soluble substance, C is the state of supersaturation that would have been reached if the substance had not come out of solution, and η is the coefficient of viscosity of the solution. The work of von Weimarn indicates that it is possible to obtain in the colloidal state any substance which normally is precipitated, and shows that the difference between colloidal and ordinary solutions is one of degree only.

The truth of this statement may be easily tested with the well-known barium sulphate precipitate. If barium sulphate is precipitated in the cold, it is found to be very difficult to filter; the particles are so small that they pass through a filter paper (a filter paper will usually retain particles as small as $5,000\text{ }m\mu$). If the barium sulphate is prepared hot, it is much more easy to filter it cleanly, because now the particles are larger in size. The reason for this is that at the higher temperature the solubility of the barium sulphate is greater and the viscosity of the water less, making δ smaller. It is even possible to obtain a barium sulphate gel. Von Weimarn states that any very sparingly soluble salt will separate as a gel if made by mixing sufficiently concentrated solutions, and recommends for the preparation of barium sulphate in this state the mixing of $3N$ aqueous solutions of barium thiocyanate and manganous sulphate. On long standing the gel takes up the ordinary form again.

A similar experiment may be tried with calcium acetate in alcohol. Calcium acetate is somewhat soluble in alcohol, but can be obtained in the form of a gel by suddenly making a supersaturated solution of it in alcohol. This is done by making a saturated aqueous solution of calcium acetate. 10 C.c. of this solution are taken and mixed by tossing from one beaker to another and back again, with 90 c.c. of 95 per cent. alcohol. A jelly sets at once. Acetone may be substituted for alcohol. For the success of this experiment it is absolutely necessary to have the aqueous solution of calcium acetate saturated. This process is one of those used for manufacturing solidified alcohol, employed as a patent fuel.

347. Classification of Colloids.—Colloidal solutions are referred to as *sols*. If the dispersion medium is water, they are called “hydrosols”, or sometimes “aquesols”. If alcohol is the dispersion medium, the colloidal solution is called an “alcosol”.

Concentrated solutions of certain colloids set to a jelly. This is called a *gel*. ✓

Sols are frequently subdivided into lyophobic (solvent-hating) and lyophilic (solvent-loving) colloids. The first class includes those sols which are readily precipitated from solution, and which then do not pass back into colloidal solution on addition of the dispersion medium. Thus a silver sol, once coagulated, cannot be made to revert to the colloidal state merely by the addition of the dispersion medium. It can, however, be re-obtained in colloidal solution by the process of peptisation (§ 349). The lyophobic sols are sometimes called also “irreversible sols”. On the other hand, the lyophilic sols are reversible. Gelatin, gum arabic, and starch are colloids of this type. They are much more stable than lyophobic sols, and are not, therefore, easily precipitated. They will easily revert to the colloidal state after precipitation, on adding the dispersion medium.

Ostwald¹ drew up a list of all the possible colloidal solutions, which is embodied in Table XCV.

TABLE XCV.—COLLOIDAL DISPERSIONS (OSTWALD)

Dispersion Medium.	Disperse Phase.	Name.
Gas.	Gas.	No colloidal dispersion. Perfect mixture always.
	Liquid.	Fog (cloud, mist) } aerosols.
	Solid.	Smoke }
Liquid.	Gas.	Foam
	Liquid.	Emulsion
	Solid.	Colloidal suspension } sols.
Solid.	Gas.	} Solid foam. Colloidally dispersed crystal inclusions. Solid emulsion.
	Liquid.	
	Solid.	
		• Colloidally dispersed eutectics. Solid sols.

It has already been stated that a colloidal solution containing separate particles, such as a colloidal solution of gold or silver, is called a sol. In addition to the classification into lyophilic and lyophobic sols, true

¹ Wolfgang Ostwald, son of Wilhelm Ostwald (who propounded the Dilution Law, etc.).

colloidal solutions may be divided into two classes, (a) colloidal electrolytes, and (b) non-electrolytic colloidal solutions.

The class of colloidal electrolytes is very interesting, and may be best illustrated by considering the soaps. If one of the higher fatty acids, such as palmitic acid, is added to water it will form a very thin film on the surface of the water. The carboxyl group has an affinity for water, and is called "hydrophilic", whereas the hydrocarbon residue attached to it is said to be "hydrophobic", since it has no affinity for water and tends to separate itself from it. The molecules will therefore orient themselves on the surface with the carboxyl groups in the water and the hydrocarbon residues sticking out from it.

If, now, caustic soda is added, a sodium salt—a soap—is formed. Palmitic acid is not dissociated to any extent, whereas the sodium salt is. The sodium ions are pulled into the water and escape, and the attraction of the sodium ions for the palmitate ions pulls the latter so strongly that they cannot remain on the surface, but are pulled beneath. They do not, however, lose their oily nature entirely, but form oily aggregates, each of which is called an "ionic micelle". In the micelle the hydrocarbon chains point to the centre as indicated in the Fig. 210 (a). (The wavy

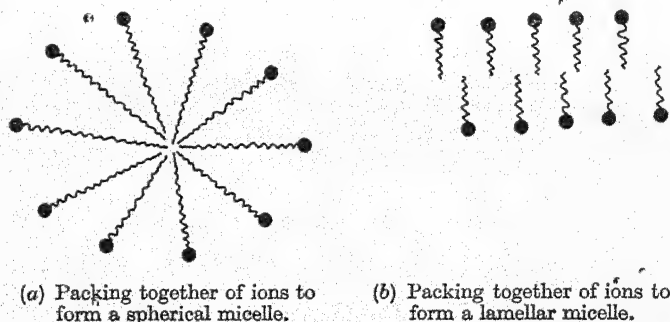


FIG. 210.—Micelle Formation. (It should be remembered that micelles have a three-dimensional structure and not two-dimensional as represented above.)

line represents the hydrocarbon portion of the molecule and the circle the COO^- portion of the molecule.) The micelle is solvated by a large number of solvent molecules. There may be ten or more RCOO^- ions in a micelle. The micelle may take up many other shapes. Among the most important is that shown in (b), Fig. 210. The solvation of the micelles is not shown in the figures. Thus, we have a colloidal solution containing sodium ions in true solution, and aggregates of palmitate ions. This is known as a colloidal electrolyte. Colloidal solutions of such substances are easily made. No special process is necessary, since the solvent itself causes the dispersion.

Many dyes are colloidal in nature, and frequently behave as colloidal electrolytes, being dragged into colloidal solution by some powerfully ionised part of the molecule.

348. Dialysis.—The observation of Graham that colloids were unable to pass through a colloidal membrane, is made use of in separating a colloid from a crystalloid. It must be emphasised that the membrane used in dialysis is quite distinct in its properties from the semi-permeable membrane used in experiments on osmotic pressure. The ordinary dialyser consists of a vessel open at both ends; one end can be covered by a parchment paper. A suitable vessel can be made by removing the bottom from a wide-mouthed bottle by means of a hot wire. The parchment should be moistened before being tied to the vessel. The dialyser is nearly filled with the colloidal solution and suspended in a vessel containing distilled water. The crystalloid gets through, leaving the colloid behind.

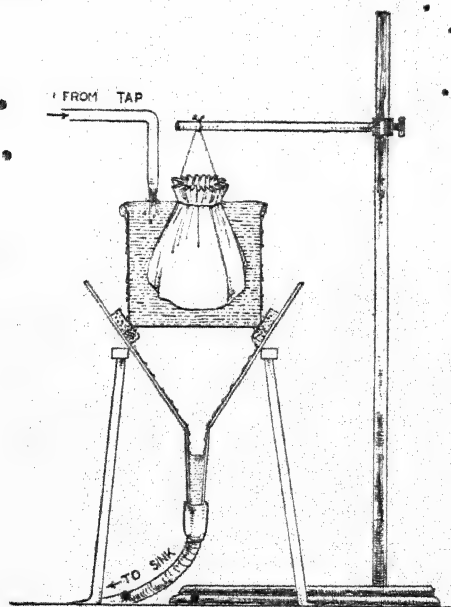


FIG. 211.—Dialyser.

A suitable dialyser is also easily made entirely of parchment by folding a moistened sheet of it round a bottle and allowing to dry. The parchment bottle will be found to retain its shape. A cord can be tied round it, and when filled with colloidal solution it may then be suspended in distilled water by means of the cord. A simple form of dialyser can be prepared by making a purse-like bag of parchment paper and suspending it as shown in Fig. 211.

Many other membranes are suitable. Recently the use of cellophane has been advocated. Collodion dialysers are also readily made by taking a test-tube and dipping it in collodion solution and allowing it to dry. The skin of collodion can then be slipped off.

Membranes of cellulose acetate have been used satisfactorily.

An interesting experiment on dialysis can be carried out by making a thin starch paste and putting it in a dialyser. Test the dialysate for glucose by means of Fehling's solution, and for starch by means of iodine. Now add to the starch some diastase and continue to test from time to time for glucose and starch in the dialysate. The action of the diastase converts the starch into a crystalloid—glucose, which will now come through the dialyser.

349. Peptisation.—If freshly prepared ferric hydroxide is treated with a small quantity of ferric chloride solution, it immediately forms a colloidal solution of a dark reddish-brown colour. The ferric chloride which has caused this dispersion is called a "peptising agent" and the process is called "peptisation". If all the ferric chloride is removed, the sol precipitates.

A similar colloidal solution is obtained with aluminium hydroxide by adding very dilute hydrochloric acid to the freshly prepared hydroxide, the amount of acid added being insufficient to convert the hydroxide completely into aluminium chloride. Stannic hydroxide sol is easily prepared by the addition of a solution of sodium stannate to one of sodium bicarbonate, washing the precipitate and suspending it in water, and then adding a small amount of ammonia.

In all these cases an electrolyte is necessary for the formation of the colloidal solution, and the stability of the substance depends on the adsorption of ions at the surface of the colloidal particles. If these are thoroughly washed with distilled water, the electrolyte can be removed and precipitation ensues. A lyophobic sol may be brought back into solution after coagulation by the process of peptisation.

It may be mentioned that the reverse behaviour is sometimes met with. Washing a precipitate repeatedly with distilled water sometimes brings it into colloidal solution. An example is the formation of vanadic acid sols.

The behaviour of colloidal solutions with electrolytes should be compared with peptisation (§ 357).

350. Preparation of Colloidal Solutions.—Many organic substances such as gum arabic, gelatin, starch, etc., form colloidal solutions merely on dissolving in water. These are the lyophilic colloids (§ 347). The same is true of colloidal electrolytes, such as the soaps, and some dyestuffs.

There are two general methods of making lyophobic sols. The first is the condensation method, in which molecularly dispersed particles are built up. The second is the reduction method, in which material in the mass is broken down into colloidal particles.

In describing the various methods under each class, experimental details will be given of the methods of preparation of certain common colloidal solutions, and the student is recommended to carry these out practically, if possible.

In the preparation of colloidal solutions it is necessary that all vessels used should be thoroughly clean, and that the materials used should be pure. It will be shown later that precipitation of a colloid is readily occasioned by addition of an electrolyte (§ 357). Hence the necessity of using materials which are known to be pure. The thorough cleansing of vessels is best carried out by steaming them out.

I. Condensation Methods.—(a) *Reduction.*—This is the usual method for preparing colloidal metals. An example is the formation of colloidal gold, or silver, by reducing a solution of a salt of the metal, much diluted, with a reducing agent, usually organic, since these do not produce ions which are inimical to colloid formation.

Zsigmondy prepared colloidal gold by first making a solution of chlorauric acid, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, containing 6 gms. per litre, and also a solution of potassium carbonate, 0.18 normal. 1,200 C.c. of twice distilled water were heated, and 2.5 c.c. of the gold solution, and then 3.5 c.c. of the potassium carbonate solution were added. The mixture was stirred and heated to 100°C . It was removed from the source of heat, and 1.0–3.0 c.c. of 0.3 per cent. formaldehyde added with stirring. A gold sol was thus produced.

Von Weimarn used Rochelle salt for reducing gold chloride, 30 c.c. of 0.1 per cent. gold chloride solution were added to 400 c.c. of boiling water. Then about 2 c.c. of 0.05 *M* Rochelle salt were added drop by drop. The boiling was continued, and after about one minute blue gold appeared, which afterwards changed to red.

Ostwald reduced gold chloride with tannin and obtained a good red gold solution. To 100 c.c. of distilled water a few drops of 0.1 per cent. gold chloride solution were added, the latter having been carefully neutralised with the calculated amount of potassium carbonate. A few drops of a 0.1 per cent. solution of tannin were added. On warming, a cherry-red colour appeared, which could be deepened by adding more gold chloride and tannin. Tannin has some protective action (see Protection of Colloids, § 359) and therefore the colloid will remain suspended longer than some others, especially if a few drops of chloroform are added to prevent the growth of mould.

Colloidal silver may be prepared as follows: To 5 c.c. of 1 per cent. silver nitrate solution, very dilute ammonia is added drop by drop until the precipitate just disappears. Dilute to 100 c.c., mix with 0.4 c.c. of a 0.5 per cent. solution of tannin. By varying the proportions and the temperature at which the mixing is carried out, sols of various colours may be obtained.

Carey Lea's silver sols will be dealt with later (§ 359).

Colloidal platinum may be obtained by the following method. 500 C.c. of chloroplatinic acid (0.1 per cent. solution) are made slightly alkaline with potassium carbonate. The solution is boiled, and then the flame is removed, and 2 to 4 c.c. of 33 per cent. acrolein added. A yellow sol is first formed, which gradually changes to black.

(b) *Oxidation*.—Colloidal sulphur may be prepared by the oxidation of hydrogen sulphide. If hydrogen sulphide is passed into a solution of sulphur dioxide in water until nearly all the odour of sulphur dioxide has been removed, the solution is found to contain sulphur, which will pass through a filter paper. The best way of dealing with this is to precipitate it all by boiling with sodium chloride, and then filtering. The precipitate is washed on the filter paper with distilled water until all sodium chloride has been removed. At the end of this process the sulphur begins to run through the paper, forming a fairly stable colloidal solution.

A good way of preparing a stable sulphur sol is to make solutions of well-washed hydrogen sulphide and sulphur dioxide. The strength of each solution is determined volumetrically, and the stoichiometrical amount of sulphur dioxide is added to a given volume of hydrogen sulphide solution.

Acidified sodium thiosulphate forms colloidal sulphur, but the sol is not very stable owing to the presence of electrolytes.

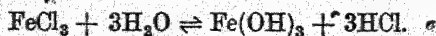
(c) *Exchange of Solvent*.—It is a general rule that if a substance A is soluble in B, but is insoluble in C, A will be thrown into suspension, usually colloidal, when a solution of A in B is added to an excess of C, the two solvents being miscible.

A sulphur sol can be made by adding a saturated solution of sulphur in alcohol to water. Phosphorus may also be obtained in colloidal solution in the same way. A good method of preparing a gamboge sol is by dissolving the substance in alcohol and then mixing with an excess of water.

A similar method is to decompose a complex salt, such as the complex potassium silver iodide obtained by dissolving silver iodide in an excess of potassium iodide, by adding much water to it. The silver iodide is then obtained as a sol.

(d) *Hydrolysis*.—This is the usual method for preparing oxide and hydroxide sols.

To prepare a sol of ferric hydroxide (or more accurately hydrated ferric oxide, the amount of hydration being uncertain), the addition of a few cubic centimetres of concentrated ferric chloride solution to much water (boiling) may be used.



To ensure stability it is advisable to dialyse the product, but if all the hydrochloric acid is removed the sol becomes unstable. The peptising

action of the acid helps to keep the hydroxide in the colloidal condition.

Zsigmondy prepared colloidal stannic acid by a similar method. A solution of stannic chloride is diluted so much that hydrolysis occurs. Wash by decantation, and peptise by means of ammonia.

Biltz prepared vanadic acid sols by the action of hydrochloric acid on ammonium vanadate. Five grams of ammonium vanadate are ground with a few drops of strong hydrochloric acid in a mortar. The product is suspended in water and filtered. The precipitate is washed well until it will pass through a filter paper, giving a red sol.

(e) *Double Decomposition*.—In many reactions where a precipitate might be expected, a colloidal solution results, and if special care is taken this may always be made the result. The application of von Weimarn's rules dealing with supersaturation gives us the correct conditions for this behaviour (§ 346).

Colloidal arsenic sulphide is readily prepared by making a 1 per cent. solution of arsenious oxide in hot water. The solution is cooled and filtered. To 200 c.c. of water saturated with hydrogen sulphide the solution of arsenious acid is added gradually, whilst a stream of hydrogen sulphide is passed through the solution. This is continued until an intense yellow sol is formed. The excess of hydrogen sulphide is removed by boiling or, better, by passing a stream of hydrogen through the solution.

Antimony trisulphide sols may be prepared in a similar way. A 0.5 per cent. solution of tartar emetic is dropped from a tap funnel into water saturated with hydrogen sulphide and through which hydrogen sulphide is passed. A beautiful orange coloured sol of good permanency may thus be made.

Manganese dioxide is an unusual colloid. Potassium permanganate, although a powerful oxidising agent, is slow in reacting with many substances. It will react slowly with ammonia to give nitrogen and manganese dioxide, the latter being formed in the colloidal state. Cuy recommends the following procedure: Heat a $M/100$ solution of potassium permanganate to boiling, and while stirring add strong ammonia solution, one drop every three minutes. There should never be a great excess of ammonia. Keep the solution at about 90°C . It turns wine red, and finally coffee brown by transmitted light, and a bluish-brown oily colour by reflected light. To test if all the permanganate has been reduced, some of the colloidal solution may be coagulated by means of common salt. If there is any violet colour there is still some unchanged permanganate. The formation of colloidal manganese dioxide is apt to be a nuisance in the Volhard method of determining manganese volumetrically. Silica sol is easily prepared by the addition of acid to sodium silicate solution (water-glass). Commercial water-glass is diluted to a density of 1.16. 75 C.c. of the mixture are taken and 25 c.c. conc. hydrochloric acid and 150 c.c. water added, and the whole is dialysed.

If the dialysis is carried too far the gel, in which colloidal silica usually exists, may form.

Silica gel can be made by mixing hot ($50^{\circ}\text{C}.$), with constant stirring, a solution of hydrochloric acid containing 10 per cent. by weight of the gas, with an equal volume of sodium silicate solution of density about 1.185. The mixture sets to a gel in about an hour, and is then broken up into small pieces and washed free from acid and salt. The washing water may be used hot to hasten the process. In drying, the water must be removed slowly. This is accomplished by passing a stream of air over the gel at $75^{\circ}\text{C}.$ and increasing the temperature to $120^{\circ}\text{C}.$, after which the temperature is slowly raised to $300^{\circ}\text{C}.$ The final product is hard and transparent, something like glass in appearance. It is largely used, when activated by heating in air at a moderate temperature for a few hours, as an adsorbent of gases, and a dehydrating agent. It is used for drying the blast in iron smelting; it is the only cheap drying agent which can be used, and dehydrated on baking, an unlimited number of times (calcium chloride loses hydrogen chloride on heating after absorption of water). It may also be used for adsorbing colouring matters and other substances from solution, in a similar way to animal charcoal.

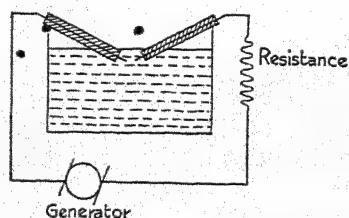


FIG. 212.—Bredig's Arc Method.

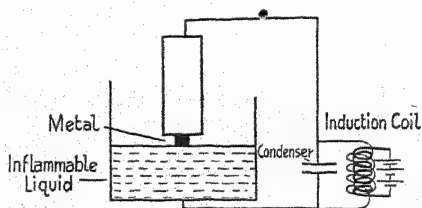


FIG. 213.—Svedberg's Method for preparing Metal Sols in Inflammable Liquids.

II. *Dispersion Methods.*—(a) *Bredig's Arc Method.*—This process consists in striking an arc beneath conductivity water between two wires made of the metal to be dispersed. In preparing gold and some other sols, however, it is found advantageous to have in the solution a trace of sodium hydroxide or potassium carbonate. The vessel in which the dispersion takes place may be cooled in ice.

Svedberg prepared metal sols of sodium, etc., in inflammable liquids, using an oscillatory discharge, produced by passing the discharge from an induction coil provided with a condenser, through the metal in contact with the liquid. Svedberg states that in the formation of sols by the electro-dispersion method the metal is first vaporised, and the sudden cooling of the vapour gives rise to the colloid. It is usually found that the sols are contaminated with some oxide if formed in water.

(b) *Mechanical Dispersion*.—Comparatively recently "colloid mills" have been devised for grinding solids into particles of colloidal size. Actually they fail to do this completely, only a few of the particles formed being of colloidal diameter. The principle of the colloid mill is, in general, that the substance to be dispersed is suspended as a coarse precipitate in the dispersion medium and the liquid is then passed through a channel in which are two plates close together, rotating at high speeds (about 7,000 revolutions per minute) in opposite directions.

(c) *Peptisation*. This has already been mentioned (§ 349). Glue, gum, gelatin, etc., are soluble in water and give colloidal solutions, but actually they are peptised by the water.

A Prussian blue sol may be prepared by the process of peptisation. A 3 per cent. solution of potassium ferrocyanide is poured slowly into a 3 per cent. solution of ferric chloride. After a few minutes the precipitate is filtered off and washed well. A 5 per cent. solution of oxalic acid is then poured through the filter until the precipitate is peptised. Then the sol is dialysed to remove oxalic acid. The sol is quite stable.

351. The Molecular Weights of Colloids.—The osmotic pressures of colloids are very small, but have been measured, and give very high figures for the molecular weight. The difficulty in this type of determination is not only that the effect is small, but that the presence of small amounts of electrolytic impurities would have a comparatively great effect on the osmotic pressure. The presence of 0.05 per cent. sodium chloride would halve the apparent molecular weight of hæmoglobin, which is about 66,000. The effect of electrolytes can, however, either be allowed for or eliminated in osmotic pressure determinations. Owing to the high molecular weight of colloidal particles the depression of the freezing point and raising of the boiling point will be small; further, if traces of electrolytes are present as impurities they will change the boiling point and freezing point to the same extent as a very much larger concentration of colloidal material. Hence these methods are of little use in the determination of the molecular weights of colloids.

The coefficient of diffusion method has been studied and applied by Herzog. The diffusion coefficient D can be shown to be given by the equation

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \quad (1)$$

where N is Avogadro's number, r the radius of the particle, and η the coefficient of viscosity of the medium. If it is assumed that the particles are spherical, then the molecular volume Mv is given by

$$Mv = \frac{4}{3}\pi r^3 N \quad (2)$$

where v is the volume of 1 gm. (*i.e.*, the reciprocal of the density), and M is the molecular weight. Substituting the value of r obtained from this equation, in equation (1) we have

$$M = \frac{1}{162\pi^2 N^2} \cdot \left(\frac{RT}{\eta D} \right)^3 \cdot \frac{1}{v}.$$

This avoids the determination of r , and was the form of the equation used.

More recently the method of sedimentation has been employed by Svedberg.

This method is really based upon the fact that the size of a particle can be determined by the rate with which it falls through a medium (gaseous or liquid). This rate is called the velocity of sedimentation. An equation connecting the velocity of sedimentation with the particle size and the viscosity of the medium was first given by Stokes (see also the determination of the charge of the electron by Millikan, in which the size of oil drops was determined by applying a modified form of Stokes' equation, § 26). This equation may be expressed in the form

$$r = \sqrt{\frac{9}{2} \cdot \frac{\eta v}{(\rho_p - \rho_a)g}}.$$

TABLE XCVI.—MOLECULAR WEIGHTS OF COLLOIDS

Substance.	Method.	Molecular Weight.
Pepsin	Sedimentation equilibrium	39,000
Insulin	" "	35,000
Hæmoglobin (horse)	" "	68,000
Serum globulin (horse)	" "	150,000
Hæmocyanin (<i>Helix pomatia</i>)	" "	6,700,000
Lactalbumin	Sedimentation velocity	17,400
Pepsin	" "	35,500
Insulin	" "	41,000
Human tuberculo- bacillus protein	" "	32,000
Hæmoglobin (horse)	" "	68,000
Hæmoglobin (man)	" "	63,000
Serum globulin (horse)	" "	167,000
Serum globulin (man)	" "	176,000
Urease	" "	480,000
Hæmocyanin (<i>Helix pomatia</i>)	" "	6,600,000

where r is the radius of the particle, η the viscosity of the liquid, v the velocity of sedimentation, ρ_p the density of the particle, ρ_d the density of the liquid, and g the acceleration due to gravity. The equation holds only for spherical particles falling freely (not near a wall).

The force of gravity is not sufficiently great to enable the size of very small particles to be determined by sedimentation. The force producing sedimentation can, however, be artificially increased by using a centrifuge. In the case of a particle falling freely through a medium under the action of gravity, two opposing forces act on the particle, the force of gravity and the frictional force which depends upon the viscosity of the medium through which the particle falls. In the case of the centrifugal force, this takes the place of the force of gravity, and the equation obtained is

$$r = \sqrt{\frac{9}{2} \cdot \frac{\eta \log_e \frac{x_2}{x_1}}{(\rho_p - \rho_d) \omega^2 t}}$$

In this equation x_1 and x_2 define the positions of a particle before and after falling; thus $x_1 - x_2$ is the distance through which the particle falls; ω is the angular velocity of the centrifuge, and t is the time occupied in falling. The other symbols have the same significance as before. If M is the molecular weight of the particle and m the mass of a colloid particle then $M = mN$ where N is the Avogadro number.

If the particles are assumed spherical $m = \frac{4}{3}\pi r^3 \rho_p$. We can therefore

use the r determined from sedimentation velocity experiments to determine M . This method cannot be used if the particles are not spherical.

Another method of using the ultra-centrifuge to determine molecular weights is the sedimentation equilibrium method. After particles have been centrifuged for some time equilibrium will be reached between the centrifugal force and the diffusion of material in a direction opposite to the centrifugal force. This will lead to a situation in which the concentration of particles at various distances from the centre of rotation will become constant. This conception was utilised by Svedberg in deriving the expression for molecular weight.

$$M = \frac{2RT \log_e (c_1/c_2)}{N (\rho_p - \rho_d) \omega^2 (x_1^2 - x_2^2)}$$

In this equation c_1 and c_2 are the concentrations of particles at points situated x_1 and x_2 cms. from the centre of rotation, and the other symbols have their former significance.

All that is necessary, then, to determine the molecular weight of the colloidal particle is to find the relationship between the concentration of

particles at two levels for a given speed of the centrifuge, the temperature being constant and known.

This equation has been used with considerable success by Svedberg, who devised an ultra-centrifuge for the purpose.¹ In this instrument fields 900,000 times the force of gravity were developed. The axis of rotation was horizontal. During the centrifuging, photographs of the cells containing the colloidal solution were taken at definite intervals on the same plate and with the same exposure. If a sedimentation equilibrium was to be studied, only those photographs taken when equilibrium had been reached would be of use, but the others would indicate whether equilibrium had been attained. After the centrifuging the cell was filled with the colloidal solution of different concentrations, and these were photographed on the same plate as before, with the machine running, in order to provide standards for judging the concentrations at various levels in the actual experiment. After the plate was developed, the intensity of blackening was determined by means of a spectrophotometer, and from these observations a curve could be drawn connecting concentration of the particles with the distance from the centre of rotation.

There is no doubt that this method of determining the molecular weights of colloids is more free from objections than others. The method can be applied to finding the size of any small particles, and for this reason in the early part of this discussion the theory was not confined to colloidal particles alone.

The ultra-centrifuge has been used extensively for the determination of the molecular weights of the proteins. Some of the results are summarised in the Table XCVI. The molecular weights of the proteins vary from about 17,000 to 10,000,000. It has been observed that the molecular weights of proteins can be expressed approximately by the equation $17,600 n = M$ where n can have the values 1, 2, 4, 6, 8, 16, 24, 48, 96, 192 and 384. Because of this relationship Svedberg suggested that proteins are built up in units of 17,600 but this view is now no longer held.

The proteins mentioned above give definite, reproducible values for the molecular weight. They are called "monodisperse" systems; apparently all the particles have the same molecular weight. There are, however, some proteins, such as gelatin and casein, of which the particles vary in size. The molecular weight of gelatin varies from 10,000 to 70,000. Such systems are said to be "polydisperse".

352. The Investigation of Colloidal Solutions by Means of the Ultra-microscope.—It will never be possible to see atoms or molecules, or even colloidal particles, by means of the best optical microscope, since it is impossible to get clear image-formation of objects smaller than the

¹ For fuller details see Svedberg and Pederson "The Ultracentrifuge". (Oxford, 1940).

wavelength of the light employed. Tyndall, however, found that small particles were able to scatter light, and that the zone of scattered light was much larger than the particle itself, and could be seen in the microscope, or sometimes even by the naked eye. The same effect is noticed when a sunbeam enters a room. The atmosphere does not ordinarily appear to be dusty, but when the beam shines through, the dust particles are shown up. A colloidal solution when illuminated by a narrow beam of light appears opalescent when viewed at right angles to the beam. This opalescence is not found with pure water,¹ and is due to the scattering of the light by the very small colloidal particles. Under the microscope the actual zones of scattered light can be seen.

This principle was used by Siedentopf and Zsigmondy in 1903 for the construction of an instrument called the "ultra-microscope". The arrangement of the instrument is shown in diagrammatic form in Fig. 214. A strong beam of light from an arc lamp, or other powerful source L, passes through a slit S, and is condensed by a system of lenses so as to come to a focus in a cell containing the colloidal solution. This cell is placed on a microscope stage and viewed through the microscope in the ordinary way. Of course, the actual contours of the particles cannot be seen; they just appear as bright spots against a dark background. But at least the number of particles can be counted, and more recently it has been possible to decide the shape of the particles roughly. Suppose that in an experiment n particles were found in a field of view of volume v c.c., then, if the sol contains b grams per cubic centimetre (determined by evaporation and weighing) of the dry substance, of density d , the mean radius r of the particles will be given by

$$r = \sqrt[3]{\frac{3bv}{4\pi nd}}$$

This assumes two things. First, that the particles are spherical, and, secondly, that the density of a substance in the colloidal condition is the same as that in bulk, and there is no proof that this is so.

The limit of visibility in the ultra-microscope depends upon the optical nature of the colloidal particles and of the dispersion medium. It is found that colloidal metals give the best results, and can be detected

¹ It has been stated by Schade and Lohfert (1930) that the purest water, when sufficiently strongly illuminated, and viewed in the manner indicated above, does show a Tyndall beam. Especially is this so when ultra-violet light is used. The phenomenon cannot be explained as due to impurities, and the suggestion is made that it is produced by the existence of a certain small fraction of the water in a highly associated condition. It should also be noted that all transparent solids, liquids and gases scatter light, even when perfectly free from suspended dust, etc. The scattering agents are the molecules themselves (see Raman spectra, § 386). The phenomenon is, however, quite different from the Tyndall beam, in which a few localised scattering agents are visible as discrete bright spots. It is necessary to bear in mind this difference between the scattering of light by colloidal and other fine particles, and by molecules.

down to a diameter of 6×10^{-7} cm. Organic particles can only be seen down to 4×10^{-6} cm.

Particles which are invisible even to the ultra-microscope are called amierons.

In 1915, Freundlich and Diesselhorst found that it was possible to distinguish between spherical and non-spherical (or rod-like) particles in the ultra-microscope. Vanadium pentoxide and benzopurpurin form rod-like particles, which give a peculiar streaky appearance when they

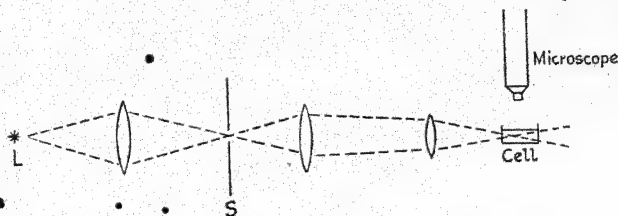


FIG. 214.—Arrangement of Ultra-microscope.

are stirred, and become doubly refracting when flowing through a tube. The anisotropy is due to the rods all moving in one direction, with their axes in line, like a raft of logs floating down a river. This should be compared with the behaviour of liquid crystals (§ 130).

By examining various sols, Freundlich and Diesselhorst showed that those of gold (red), silver, platinum, arsenic sulphide and gamboge were spherical. The particles of aged ferric oxide and blue gold sols were disc shaped, whereas vanadium pentoxide, tungstic acid, and many colloidal dyestuffs gave rod-like particles.

Many colloidal particles have been shown by direct experiment with X-rays to be crystalline in nature, but, according to Kohlschutter's work, a large number of substances tend to have particles of definite form and shape, and yet are not crystalline. These are called "somatoids".

353. The Colours of Colloidal Solutions.—The colour of a sol will depend on its particle size, for upon this depends the nature of the light scattered by the particles. Like the colour of the sunset, the colour of colloidal solutions is due to light scattering. It should be possible, therefore, to calculate the size of particle required to give a certain colour, assuming that the particle is spherical in form. This has been done by Mie, and his results have been verified experimentally by Schaum with silver sols, and by Feick with mercury sols. There is satisfactory agreement between the calculated and observed results, but this is not always the case.

The colour in many other cases is decided also by the shape of the particles, and at present no calculation has been made which takes this

into account. Frequently, the specific absorption of light by the colloidal particles is of greater importance than the scattering in determining the colour.

354. The Brownian Movement.—In 1827 the botanist Robert Brown discovered that grains of pollen placed in water moved about ceaselessly. The cause of this motion was not suspected for many years, being at first ascribed to convection currents in the liquid. When colloidal solutions were examined under the ultra-microscope it was

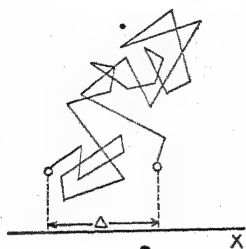


FIG. 215.—The Brownian Movement.

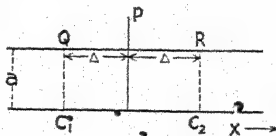


FIG. 216.

found that the particles in these solutions too were in constant motion, traversing no definite set path, but going in zig-zag directions all over the field of view. It was shown as the result of work by Wiener (1863), Ramsay, Delsaulx and Carbonelle, Gouy (1888) and others that the motion was independent (or nearly so) of the nature of the colloidal particle, but was more rapid the smaller was the particle, and the less viscous the solution. Wiener was the first to state that the movement was due to molecular motion. The small colloidal particles are knocked about by collision with the molecules of the dispersion medium.

At first sight it would appear difficult to make any accurate observations on the motion, which is so haphazard. However, it is possible to calculate what the probable displacement of a particle will be after a given time. This displacement may be conveniently measured as a projection of any axis we may choose to take, x (see Fig. 215).

Take now a cylinder of the sol of area of cross-section a (Fig. 216). Consider a plane P in it, and let the concentration of sol be c_1 at a distance Δ to the left of P (i.e., at the plane Q) and c_2 at a similar distance to the right of P (i.e., at the plane R). We shall consider only the components of the particles parallel to the x -axis, as we wish to calculate the number of particles which will cross from one side of the plane P to the other in the small time t . Let the mean value of the displacements parallel to the x -axis in the time t be Δ . The particles arriving at P from the left are only those whose distance from the plane P is less than Δ . Moreover, only half of these may be taken as moving towards the plane, since by probability half of them will be moving in

the opposite direction. Similarly for those moving from the right across P. The number of particles crossing P in time t is therefore

$$\frac{1}{2}a\Delta (\text{mean concentration in region PQ} - \text{mean concentration in region PR}),$$

$$= \frac{1}{2}a\Delta \frac{(c_1 - c_2)}{2} \quad (1)$$

The value of the concentration gradient, $\frac{dc}{dx}$, is given by

$$-\frac{dc}{dx} = \frac{(c_1 - c_2)}{2\Delta} \quad (2)$$

Hence, substituting for $(c_1 - c_2)$ in (1), the number of particles crossing P in one second is

$$- \frac{1}{2} \frac{a}{t} \Delta^2 \frac{dc}{dx} \quad (3)$$

Now, the *diffusion coefficient* D is defined as the number of particles passing in unit time across a plane of area 1 sq. cm., the concentration gradient being unity. Hence, putting $a = 1$, and $\frac{dc}{dx} = 1$, we have

$$D = \frac{1}{2} \frac{\Delta^2}{t} \quad (4)$$

Hence, the square of the mean displacement of the particles, Δ^2 , is proportional to the time t , during which the displacement occurs.

It is possible from this to deduce a relationship between the coefficient of diffusion, the size of the particles, and the viscosity of the liquid. The derivation is due to Einstein. If the velocity of the moving particle is u , k is the force causing its motion, and F the frictional resistance.

$$u = \frac{k}{F}$$

If a solution of concentration c gm.-mols. per unit vol. is considered, we have for the diffusion across a given plane

$$u = \frac{1}{cN} \cdot \frac{K}{F} \quad (5)$$

where K is the total force acting on all the particles, and N is Avogadro's number (cN will be the number of particles in unit volume, since N is the number of molecules in 1 gm.-molecule). The force acting on the particles is the gradient of osmotic pressure, P .

$$\therefore K = - \frac{dP}{dx}$$

The relationship between the pressure P and the concentration c is approximately

$$P = RTc$$

Hence,
$$K = -RT \frac{dc}{dx} \quad (6)$$

Substituting for K in (5), we get

$$uc = - \frac{RT}{NF} \cdot \frac{dc}{dx} \quad (7)$$

The relationship between the frictional resistance F to the motion of a particle of radius r , in a liquid of viscosity η , is

$$F = 6\pi\eta r \quad (8)$$

Substituting this value of F in (7), we have

$$uc = - \frac{RT}{6\pi\eta r N} \frac{dc}{dx} \quad (9)$$

uc is the amount of substance passing through unit section in unit time;

when $-\frac{dc}{dx}$ is equal to unity, this quantity uc is the diffusion coefficient

D . Hence

$$D = \frac{RT}{6\pi\eta r N} \quad (10)$$

We can now substitute this value of D in (4), obtaining

$$\Delta^2 = \frac{RTt}{3N\pi r \eta} \quad (11)$$

Now, all the quantities can be measured in this equation except N , and hence the method can be used for determining Avogadro's number.

This equation has been tested by Perrin and others, whose results are given in Table XCVII.

TABLE XCVII.—VALUES OF AVOGADRO'S NUMBER FROM EXPERIMENTS
BASED ON THE BROWNIAN MOVEMENT

Nature of Colloidal Solution.	Radius of Particles in μ .	$N \times 10^{-23}$.
Gamboge in water	0.367	6.9
Gamboge in 35 per cent. sugar solution	0.212	5.5
Mastic in water	0.52	7.3
Mastic in 27 per cent. urea solution .	5.50	7.8
Gamboge in 10 per cent. glycerin solution	0.385	6.4

355. The Distribution of Colloidal Particles under Gravity.—After standing for some time a colloidal solution will be found to deposit the colloid. It is clear that by the very action of gravity alone the greater number of particles will be found at the bottom of the vessel, and that their vertical distribution will be exponential. Assuming that the particles obey the gas laws, the distribution of particles will be the same as the distribution of the atmosphere, the density of which is greatest near the earth's surface. It can be shown quite easily that if D_1 and D_2 are the densities of particles (*i.e.*, number of particles in a given volume) at heights h_1 and h_2 respectively, and if M is their molecular weight, and T the absolute temperature

$$\log_e \frac{D_1}{D_2} = \frac{Mg(h_2 - h_1)}{RT}.$$

Instead of the molecular weight M , we may write for a colloidal solution mN , where m is the mass of one particle (or the mean mass of the particles) and N is Avogadro's number. For m we may put VD , where V is the volume of a particle and D is the effective density of the colloid in the solution which (on account of the upthrust) is equal to its absolute density D_c minus the absolute density of the dispersion medium, D_m . Hence,

$$\log_e \frac{D_1}{D_2} = \log_e \frac{n_1}{n_2} = \frac{NV(D_c - D_m)g(h_2 - h_1)}{RT}$$

n_1 and n_2 being the average number of particles in any given volume at the two heights.

Perrin also used this equation to calculate N . He determined n_1 and n_2 by direct counting, having taken a photograph of the particles at the two levels chosen. The distance between the levels was determined by the focussing screw on the microscope, the readings being taken when the two levels were focussed. Perrin prepared particles of gamboge and of mastic of any desired size by a centrifugal machine. He measured their volumes and diameters by several methods which all gave results agreeing with each other. Knowing the volume of the particles he could calculate N . This he found to be 6×10^{23} , which agrees closely with the value obtained by quite different methods, and thus indicates the accuracy of the arguments about the motion of colloidal particles (see § 89).

356. Electrical Properties of Colloids.—If the lower part of a U-tube of the form shown in Fig. 217 is filled with ferric hydroxide sol, and then distilled water is poured over this, it is found that when a high potential is applied between electrodes placed in the water, the boundary between the colloid and the distilled water begins to move. This movement must indicate that the colloidal particles themselves are electrically charged, and behave somewhat as ions do under similar circumstances (see Lodge's experiment, § 308). This motion of colloid

particles under the action of an electric field is called *cataphoresis*. It has been suggested that since this term seems to indicate motion towards the cathode, which is not by any means always the case, a better term would be *electrophoresis*.

If this experiment is tried with various colloids, it is found that some move towards the anode and some towards the cathode. Hence some colloids bear a positive and others a negative charge. The majority of sols are charged negatively. The metals and the sulphides are the chief members of this class. The metallic hydroxides and oxides, and basic dyestuffs, are positively charged. The Table below shows the two classes.

The absolute mobility of the particles can be determined in the same way as the absolute velocity of ions by the moving boundary method. The result obtained for colloidal gold or silver is in the neighbourhood of $2 - 4 \times 10^{-4}$ cm. per sec. for a potential gradient of 1 volt per cm. This is also approximately the absolute velocity of organic ions of high molecular weight, and it has been suggested by Hevesy that there is not a great difference between these two classes, because for a colloidal particle the mass and the charge have increased in approximately the same proportions. The chief difference will be caused by viscosity.

In what way is this charge obtained? In the case of the electrolytic colloids, such as sodium palmitate and the soaps in general, the answer is that ions are produced, and the charge is definitely ionic. But this explanation will not hold for non-electrolytes. It was thought at first that the charge was caused by friction, but this has not proved to be the

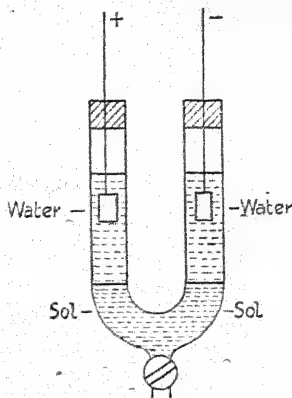


FIG. 217.—Apparatus for Cataphoresis.

TABLE XCVIII.—CHARGES ON COLLOIDS DISPERSED IN WATER

Positively Charged.	Negatively Charged.
The hydroxides, <i>e.g.</i> , $\text{Fe}(\text{OH})_3$, $\text{Cd}(\text{OH})_2$, $\text{Cr}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, etc.	The sulphides, <i>e.g.</i> , As_2S_3 , Sb_2S_3 , CdS , etc.
The oxides, <i>e.g.</i> , TiO_2 , etc.	The metals, <i>e.g.</i> , Ag, Au, Pt.
Basic dyes.	Organic colloids, <i>e.g.</i> , gum arabic, starch, gamboge.
	Acid dyes.

correct explanation. The probability is that the colloidal particles adsorb ions present in the dispersion medium. This view was put forward by Hardy, who showed that it was possible to change the sign of the charge on a colloid by placing it in an environment of ions of an opposite sign to that which it had. Thus mastic when suspended in water is found to have very little charge indeed, but when placed in an

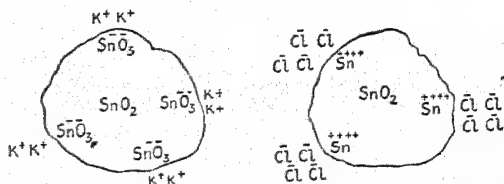


FIG. 218.—Positive and Negative Stannic Oxide Particles.
[After Fig. 13 of Dr. E. S. Hedges, *Chapters in Modern Inorganic and Theoretical Chemistry* (Edward Arnold & Co.).]

acid solution it becomes charged positively, presumably because of adsorption of hydrogen ions; and in alkaline solution it becomes charged negatively, owing to adsorption of the negatively charged hydroxyl ions.¹ This would also explain the fact that the solution as a whole is always electrically neutral. If the charge were frictional, the whole liquid should bear a charge.

This is also shown by mobility experiments with silver sols in the presence of aluminium sulphate (Svedberg, 1907, and others). The mobility decreases as the negatively charged silver ion adsorbs more of the positively charged Al^{+++} , until it can actually be reversed. At a certain point the silver particles will bear no charge.

This is called the *isoelectric point*. At this point the colloid coagulates. This process of coagulation is not as a rule instantaneous, and hence it is sometimes possible to change the sign of the charge on the colloidal particle by passing through the isoelectric point rapidly.

It is now seen why it is necessary not to dialyse colloids too much. If all the ions were washed away, the particles would be left uncharged and would coagulate.

The origin of the charge on the particles is still a matter of some doubt. We know that ions are adsorbed, but where do they come from? It is thought that an electrical double layer is formed on the surface of the particle (Helmholtz). Take the case of stannic oxide. This can be peptised by potassium hydroxide to give a negatively charged sol and by hydrochloric acid to give a positively charged sol. In the former

¹ The same effect is noted with egg albumen, but the explanation is probably different. All proteins are complex amino-acids of the type $NH_2 - [X] - COOH$.

They form ions $+NH_3 - [X] - COOH$, $NH_3 - [X] - COO^-$, or $NH_2 - [X] - COO^-$. The first is formed in acid solution, the last in alkaline solution. The second or Zwitter-ion (§ 333) is present at the isoelectric point. The lyophilic colloids do not precipitate at this point, but their solubility is a minimum there.

"ISOELECTRIC POINT"

TABLE XCIX.—VARIATION OF MOBILITY OF SILVER SOL WITH ADDITION OF Al^{+++}

Gms. of Al^{+++} added per 100 c.c. of Ag Sol.	Mean Mobility. cm./sec./volt.
0	2.0×10^{-4}
1.7×10^{-5}	1.28×10^{-4}
3.5×10^{-5}	1.03×10^{-4}
5.2×10^{-5}	0.26×10^{-4}
6.1×10^{-5}	0,
(Direction reversed)	
6.9×10^{-5}	-0.42×10^{-4}
8.7×10^{-5}	-0.61×10^{-4}
17.3×10^{-5}	-1.56×10^{-4}

process it is assumed that the oxide reacts with the hydroxyl ion to give the stannate ion and this is adsorbed on the particle leaving the potassium ions outside. The result of this is the formation of an electrical double layer at the particle medium boundary. The layer is made up of stannate ions on the particle side and potassium ions on the medium side. Due to the adsorption of the stannate ions the particles have a negative charge. If hydrochloric acid is the peptising agent the hydrogen ion reacts with the stannic oxide to give a stannic ion which is adsorbed on the particle side of the double layer giving the particle a positive charge. The chloride ions from the hydrochloric acid remain in the medium.

Since the particles of a colloidal solution are charged, and move under the influence of a field, it follows that if the particles are kept still the dispersion medium must move. This movement is called *electro-osmosis*. A suitable apparatus for demonstrating this is shown in Fig. 219. A U-tube has one limb closed with a tap, and is provided with a sealed-on capillary tube C.

The particles are made into a porous block shown in the centre of the tube. This block may consist, say, of porous earthenware, when the electro-osmosis due to the clay particles is measured. The vessel is filled with water until it just enters the capillary. On passing a current between the electrodes A and B, water will rise or fall in the limb T according to the direction of the current. This is then arranged so that the liquid rises in T. The rate at which the water moves along the capillary C, is a measure of the electro-osmosis.

357. Coagulation of Colloids by Electrolytes.—If an electrolyte is added to a sol, precipitation frequently occurs. This coagulation of

colloids by electrolytes, to which reference was occasionally made in the description of the methods of preparation of colloids (§ 350), was investigated by Hardy and Schulze, Freundlich, Zsigmondy, and others.

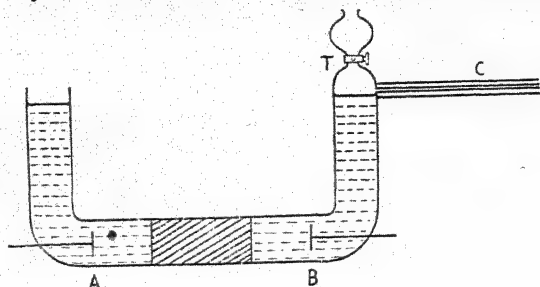


FIG. 219.—Apparatus for Electro-osmosis.

If our view as to the nature of the charge on the particles is correct, it follows that coagulation will be brought about by the agency of an ion bearing an opposite charge to that on the particle. This was found to be the case. In the precipitation of the positively charged ferric hydroxide sol, it is the anion which is of importance. It does not greatly matter what the cation is. It is known that adsorption of the ions of the added electrolyte occurs when coagulation takes place, since the coagulated colloid always drags down with it some of the precipitating substance. A certain minimum amount of electrolyte is necessary to bring about coagulation, and this amount varies with the valency of the added ions. The following Table gives the minimum amounts of various electrolytes required to coagulate a given amount of arsenious sulphide sol. The amount is expressed in millimols of electrolyte required per litre of sol.

The Law of Hardy and Schulze states that *the coagulating effect of an ion depends upon its valency*. It is clear that the Law is satisfied by the

TABLE C.—COAGULATION OF As_2S_3 SOL (1.85 gms./litre)

Univalent Cations.	Coag. Value.	Bivalent Cations.	Coag. Value.	Tervalent Cations.	Coag. Value.
LiCl . . .	58	MgSO ₄ . . .	0.81	AlCl ₃ . . .	0.093
NaCl . . .	51	MgCl ₂ . . .	0.72	Al(NO ₃) ₃ . . .	0.095
KCl . . .	49.5	CaCl ₂ . . .	0.65	$\frac{1}{2}$ Al ₂ (SO ₄) ₃ . . .	0.096
KNO ₃ . . .	50	SrCl ₂ . . .	0.63	Ce(NO ₃) ₃ . . .	0.080
$\frac{1}{2}$ K ₂ SO ₄ . . .	65.5	BaCl ₂ . . .	0.69	Mean . . .	0.091
Mean . . .	54.8	ZnCl ₂ . . .	0.68		
		(UO ₂)(NO ₃) ₂ . . .	0.64		
HCl . . .	31	Mean . . .	0.69		
$\frac{1}{2}$ H ₂ SO ₄ . . .	30				

data in Table C. The coagulating powers of univalent cations are all approximately the same, as are those of bivalent and tervalent cations. Yet between the classes there are great differences. Much more of a univalent cation is required than of a bivalent, and much more of a bivalent than of a tervalent ion. Taking a rough average of the figures quoted, it is seen that univalent cations have a coagulation figure of about 54.8 (omitting the figures for the acids, which are obviously out of place); that for bivalent cations is about 0.69, and for tervalent cations about 0.09.

If electrolytes can bring about coagulation, it is obvious that if two oppositely charged colloids are mixed, coagulation of both will occur, if the total amount of charge on each is equal. If not, partial coagulation only will occur.

The coagulation of a colloid by the addition of an electrolyte is by no means as simple as the above account would lead one to think. It has been found that the amount of electrolyte required to precipitate a given amount of a colloid seems to depend upon the rate at which it is added. There are many complicating factors.

358. Protection of Colloids.—If a stable organic colloid, such as gelatin, is added to a metal sol, the latter may be prevented from coagulating on the addition of an electrolyte. Also, the sol may now be evaporated to dryness, and on treatment with water will redissolve as a colloidal solution. Thus its behaviour is altered from that of an irreversible colloid to that of a reversible one.

Zsigmondy, in order to measure the relative protecting powers of organic colloids, originated the principle of the *gold number*. The gold number of a protective colloid is the quantity in milligrams of the added colloid which is able to protect 10 c.c. of a red gold sol (0.5 to 0.06 gm. of gold per litre) from coagulation by the rapid addition of 1 c.c. of a 10 per cent. solution of common salt. The gold sol must be specially prepared according to a given recipe. It is clear from the nature of this

TABLE CI.—GOLD NUMBERS

Sol.	Gold Number
Gelatin	0.005–0.01
Casein	0.01 –0.02
Hæmoglobin	0.03 –0.07
Albumen	0.1 –0.2
Gum arabic	0.15 –0.25
Dextrin	6 –20
Potato starch	20 –25
Colloidal SiO ₂	No protective action.

definition that the gold number is not a very accurate constant for a colloid. Some gold numbers are given in Table CI.

Protective action is a very important phenomenon. It enables colloids to be kept when otherwise spontaneous change would take place. Thus, if potassium iodide is added to mercuric chloride solution, a red precipitate of mercuric iodide is formed. It is well known that the yellow form is produced first and that it immediately changes to the red form. If now potassium iodide is added to a solution of mercuric chloride to which some gelatin has been added, a yellow colloidal form of the iodide is produced which does not coagulate, and may be kept for years.

By this means it has been found possible to prepare colloidal solutions of the metals of high concentration. Carey Lea prepared silver sols containing 99 per cent. silver by reducing silver nitrate with mixtures of ferrous sulphate and sodium citrate. The organic matter which they contain acts as a protective colloid for the silver. Such sols are used in medicine for intravenous injection, or as an ointment.

Paal and Amberger have used sodium protalbate and sodium lysalbate (decomposition products of the proteins) for protection of metallic sols with very good results.

In the commercial preparation of ice cream, a little gelatin is added as a protective colloid, to give the cream a smooth taste. If it were not added, small gritty crystals of ice and lactose would separate.

359. Colloids and Analysis.—In qualitative analysis, colloidal solutions are frequently met with. In the precipitation of the sulphides in Group II by hydrogen sulphide, colloidal sulphur is frequently formed. We now see how this may be removed. The addition of an electrolyte will cause coagulation. It is not permissible to add any electrolyte at will, but ammonium chloride can be added. The addition of this substance also helps to ensure complete precipitation and easy filtration of the sulphides of Group IV. One is always told to remove organic matter before starting on a qualitative analysis. This is because the organic substance may form a protective colloid, and prevent the complete precipitation of the various group precipitates.

In the separation of zinc from manganese by "dissolving" the zinc hydroxide in sodium hydroxide, it is very probable that sodium zincate is not formed at all, but that the zinc hydroxide is peptised by the alkali, since on passing the solution through an ultra-filter¹ zinc hydroxide is kept back.

This matter is of great importance in gravimetric analysis. One of the chief sources of error here is in the adsorption of substances by the precipitate, and it is often a very difficult matter to remove these adsorbed impurities. Adsorption will depend upon particle size (§ 360)

¹ Ultra-filters will retain colloidal particles. Ultra-filters are prepared by impregnating filter papers with collodion.

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being greater the smaller the particle, and this in turn is governed by von Weimarn's rules (§ 346). It is therefore clear that the temperature and concentration of the reactants are important considerations in gravimetric analysis. To prevent adsorption as much as possible, the precipitation should be carried out at the boiling point and fairly concentrated solutions should be used.

Colloids have great application in industry, particularly in adsorption. Large quantities of silica gel are manufactured for use in adsorption of gases, for which it is as effective as charcoal. It is probable that dyeing is a colloidal process. The treatment of sewage is also a colloidal problem, since the impurities are largely present in the form of sols. Colloidal chemistry is also of importance in the study of the soil, in the manufacture of paints, in tanning. It also has a great deal to do with biological processes, but a full treatment of these would be outside the scope of this book.

360. Adsorption.—The Gibbs Adsorption Law.—When the concentration in the interfacial layers between two phases is greater than in the bulk of either phase, then the substance is said to be adsorbed at the interface.

Many solid substances have the power of adsorbing moisture. Particularly do glass and porcelain possess this property. Some porous substances have the power of adsorbing gases.

Adsorption is a surface phenomenon, and hence it will increase in importance as the particles are made smaller, for then a larger surface is presented by a given substance. Adsorption differs from absorption in being confined largely to the surface of the adsorbent. It is observed at the surface of a solution. It was shown theoretically by Gibbs that those substances which lower the surface tension of a solvent in which they are dissolved become concentrated in the surface layer, whilst the concentration of substances which raise the surface tension is less in the surface layer than in the bulk of the solution.

Thus when many inorganic salts are dissolved in water they increase the surface tension slightly, so that the concentration of the salt in the top layer of the solution will be less than in the bulk of the liquid. On the other hand, many organic substances, such as esters, aldehydes and ketones, lower the surface tension, and are therefore more concentrated in the top layer than in the bulk of the solution.

The mathematical expression, derived by Gibbs, governing this variation in concentration is

$$-S = \frac{C}{RT} \cdot \frac{d\gamma}{dC},$$

where S is the excess of solute in the surface layer; the sign indicates whether there is actually an excess or a deficit, C is the concentration of solute if equally distributed, R is the gas constant, T is the absolute

temperature, and γ is the surface tension. $\frac{d\gamma}{dC}$ is, of course, the variation of surface tension with concentration, and can be obtained by plotting γ against C ; $\frac{d\gamma}{dC}$ is the slope of this curve at the point at which the conditions are those of the experiment.

A direct experimental proof of the Gibbs equation was obtained by McBain and Swain. They used a rapidly moving microtome blade to remove the surface layer of solutions of phenol and hydrocinnamic acid and sodium chloride. It was found that there were differences between the concentration of the solute in the surface layer and that in the bulk of the solution. The difference found was that which would be expected from the Gibbs equation.

Actually the Gibbs Adsorption Law was first derived for the solution of gases in liquids. If a gas, on solution in a solvent, increases the surface tension, the concentration of gas in the top layer of the solution will be less than in the bulk of the solution, and if, on solution, the surface tension is decreased, the concentration will be greater in the surface layer. The equation here is

$$-S = \frac{p}{RT} \cdot \frac{d\gamma}{dp},$$

where p is the partial pressure of the gas, and the other terms have their previous significance. Again, this formula has not been proved quantitatively, though it is known qualitatively that such an adsorption takes place.

As the Gibbs equation shows, low temperatures will favour adsorption. There need not be chemical change when adsorption takes place, though frequently there appears to be some such change. It is a matter of great importance in connection with heterogeneous catalysis (§ 374).

Many solids adsorb gases. The removal of such adsorbed layers of gas is a problem which is of frequent occurrence. It has already been mentioned that glass and porcelain take up moisture. This layer must be removed before carrying out any quantitative experiments involving change of temperature, as otherwise the mass of the adsorbed moisture at the end of the experiment may be different from that at the start. The removal may be effected by heating the vessel to redness, and allowing it to cool in a desiccator. In the construction of discharge tubes for studying the conductivity of gases and the production of spectra, and in the manufacture of wireless valves, where a great deal depends upon the maintenance of a high vacuum, it is necessary to "outgas" the various metal parts and the glass of the tubes by heating to redness *in vacuo*. Otherwise, when the vacuum in the tube had been created, the gas would slowly be given up by the metal parts and the glass, causing an appreciable pressure.

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The removal of adsorbed gases also plays an important part in paint manufacture. Unless the solid particles of colouring matter are directly in contact with the linseed oil in which they are suspended, the paint will not adhere well to the surface to be painted, and will have a poor covering power. The gases are removed by continued grinding with the oil.

The process of adsorption of gases by solids, however, has its uses, as well as its disadvantages. Some porous substances, such as charcoal (particularly coco-nut charcoal) adsorb gases very readily. Reference to this has already been made (§ 241) in connection with the removal of the last traces of gas from an "exhausted" tube. The adsorption of gases by silica gel has already been mentioned.

The adsorption of colouring matters from solution by animal charcoal is an example of the same phenomenon, and is a process of great technical importance in the refining of sugar. The brown sugar solution is warmed and allowed to stand in contact with animal charcoal for some hours. The colourless solution is then run off.

Adsorption is frequently a nuisance in gravimetric and qualitative analysis. Reference has already been made to the contamination of precipitates by adsorbed substances (§ 131), and to the errors caused in analytical results. Even thorough washing does not remove the impurities completely. In qualitative analysis, the hydroxides of zinc and calcium are frequently adsorbed by ferric hydroxide, so that if the first two metals are only present in traces in the original iron-containing mixture, they may not be detected, being completely adsorbed by the ferric hydroxide.

Ferric hydroxide is a good adsorbent for arsenic from sodium arsenite, and is used as an antidote for arsenic poisoning.

361. Distinction between Absorption and Adsorption.—The essential difference between absorption and adsorption lies in the fact that the latter is a surface phenomenon, and the former concerns the whole mass of the adsorbent. In practice, it will be expected that in the case of adsorption, equilibrium will be attained rapidly, whereas in the case of absorption it will be reached more or less slowly.

The experimental distinction may be shown by an experiment carried out by McBain (1909). When charcoal takes up hydrogen at the temperature of liquid air, both absorption and adsorption appear to occur. Charcoal saturated with hydrogen was placed in a vessel which could be exhausted, and which was provided with a manometer. When the vessel was exhausted, the hydrogen was removed from the charcoal in two stages. Some was removed rapidly, the rest very slowly. The first amount removed was that adsorbed on the surface, the second that absorbed by the interior of the charcoal. Similar phenomena were observed when the reverse change took place. An "outgassed" charcoal was placed in an atmosphere of hydrogen. Within two minutes 99 per cent. of the hydrogen that could be taken up by the charcoal was

adsorbed. The remaining 1 per cent. was taken up slowly, corresponding to a slow diffusion into the interior of the charcoal.

McBain proposed the use of the term *sorption* to cover the whole phenomenon of the taking up of a gas by a solid. The surface effect is *adsorption*, the solution in the interior of the substance is *absorption*. These terms are universally accepted.

362. Determination of the Amount of Sorption.—This is usually done by first freeing the substance from gases already taken up by heating *in vacuo*. A weighed amount of the substance is taken. After evacuating, and cooling, a measured amount of gas is admitted, and the pressure and volume noted after waiting until no more gas is taken up. From these values the amount of gas taken up can be found.

363. The Freundlich Adsorption Isotherm.—If x is the mass of gas adsorbed, and m the mass of the adsorbent, and p is the pressure of the gas,

$$\frac{x}{m} = ap^{\frac{1}{n}},$$

where a and n are constants. This relationship was obtained empirically by Freundlich, and is known as the *Freundlich adsorption isotherm*. It has no theoretical significance, and holds only for medium gas pressures.

In the case of adsorption from a solution, the equation becomes

$$\frac{x}{m} = ac^{\frac{1}{n}}$$

where c is the equilibrium concentration of the adsorbed substance in the solution.

Taking logarithms, we have

$$\log x - \log m = \frac{1}{n} \log c + \log a,$$

so that if $\log x$ is plotted against $\log c$, a straight line should be obtained.

The adsorption isotherm bears a certain formal similarity to the Distribution Law (§ 261). If the concentration of a substance distributed between two immiscible liquids is c_1 in the first substance and c_2 in the second, and if n is the degree of association of the solute in the second solvent,

$$\frac{c_1^n}{c_2} = k,$$

where k is a constant.

Hence,

$$\begin{aligned} c_1 &= \sqrt[n]{kc_2} \\ &= k_1 c_2^{\frac{1}{n}}. \end{aligned}$$

It will be seen that this is very similar to the adsorption isotherm. It cannot, however, be argued that the value of n indicates the extent of association in the adsorbed layer.

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The following data for the adsorption of argon by coco-nut charcoal at -78.3°C . illustrate the law.

TABLE CII.—ADSORPTION OF ARGON BY COCO-NUT CHARCOAL AT -78.3°C . (Miss Homfray, 1910).

$$a = 3.698; \frac{1}{n} = 0.6024.$$

p (cm. of Mercury).	$\frac{x}{m}$ (Obs.).	$\frac{x}{m}$ (Calc.).
5.42	9.9	10.2
9.84	15.4	14.7
12.9	18.6	17.3
21.8	24.0	23.7
56.4	39.4	41.9

Adsorbed substances, especially gases, frequently show enhanced activity. Thus hydrogen adsorbed on palladium will act very much like nascent hydrogen. It will precipitate mercury from mercuric chloride, and reduce ferric chloride. This is of importance in connection with the theory of catalysis (§ 374).

364. Langmuir Isotherm.—Langmuir derived an adsorption isotherm on the basis of the kinetic theory. If μ is the number of gas molecules striking 1 sq. cm. of the adsorbing surface per second, and if a fraction α of these molecules adhere to the surface which has already a fraction θ covered by gas molecules, then the rate at which molecules are adsorbed is $(1 - \theta) \alpha \mu$. Simultaneously adsorbed molecules are desorbed, and the rate of desorption is proportional to the fraction covered; the rate of evaporation is, therefore, $v\theta$ where v is a constant. At equilibrium the processes of adsorption and desorption are proceeding at equal rates so:

$$(1 - \theta) \alpha \mu = v\theta;$$

then

$$\theta = \frac{\alpha \mu}{v + \alpha \mu}$$

If it is assumed that the gas molecules form a layer one molecule thick on the surface then the fraction of surface covered is proportional to the amount of gas adsorbed per gram of the adsorbent, that is

$$k\theta = \frac{x}{m} \text{ and } \theta = \frac{x}{km}$$

where k is constant, x is the amount of gas adsorbed, and m the weight of adsorbent. The constant μ is proportional to p the pressure

of the gas and, therefore, $\mu = k_1 p$. Substituting these values and equating the values for θ gives:

$$\frac{x}{km} = \frac{ak_1 p}{v + ak_1 p}$$

or

$$\frac{x}{m} = \frac{akk_1 p}{v + ak_1 p}$$

Dividing the numerator and the denominator of the term on the right-hand side by v gives

$$\frac{x}{m} = \frac{\frac{a}{v} k k_1 p}{1 + \frac{ak_1 p}{v}}$$

a, k_1 and v are all constants and so $\frac{ak_1}{v}$ can be written equal to k_2 so

$$\frac{x}{m} = \frac{k k_2 p}{1 + k_2 p}$$

This equation is known as Langmuir's Adsorption Isotherm. It may be rearranged to give

$$1 + \frac{x}{m} = \frac{1 + k_2 p}{k k_2 p}$$

and

$$p \left/ \frac{x}{m} \right. = \frac{1}{k k_2} + \frac{p}{k}$$

Plotting $p \left/ \frac{x}{m} \right.$ against p should give a straight line. McBain and Brittain found that this was reasonably true for ethylene at pressures up to about 40 atms., at 0°C. and 45°C.

The Langmuir isotherm frequently does not agree with experimental results. This is because in deducing the isotherm the adsorbing solid is assumed to be a uniform adsorbent. Actually surfaces are non-uniform. Further it is assumed that the gas is adsorbed as a monolayer. This condition does not always hold in practice.

365. Types of Adsorption.—There appear to be two main types of adsorption, physical (also called van der Waals adsorption) and chemisorption. The difference between these types of adsorption lies in the nature of the forces causing the gas molecules to adhere to the surface. In physical adsorption the gas is held on the surface by the so-called van der Waals forces. These involve weak intermolecular attractions and are the forces that cause the molecules in a liquid to stay together. The van der Waals forces are characterised by low heats of adsorption (1 kg.-cal. per mole). Physical adsorption is easily reversed

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either by raising the temperature or lowering the pressure. With chemisorption the gas molecules are held on the solid surface by chemical bonds formed between the gas molecules and molecules or atoms on the solid surface. An example of such adsorption is the adsorption of oxygen on tungsten. The heats of adsorption are high (50–100 kg.-cal. per mole) and the process is reversed with difficulty, and only after heating to high temperatures.

366. Adsorption Indicators.—Within recent years various dye-stuffs, which owe their use to adsorption, have been introduced as indicators, particularly in silver titrations. Thus potassium bromide is conveniently titrated with silver nitrate, using eosin as an indicator. When the silver nitrate is run into the bromide a precipitate of silver bromide is produced, which, however, can adsorb either silver or bromide ions, the latter preferentially. It can also adsorb the dye eosin. When silver ions are adsorbed they are adsorbed as their eosin salts, which are brick-red. Thus so long as there is excess bromide present, the bromide ions will be adsorbed in preference to silver, and the solution retains the colour of the eosin, a pinkish-yellow. As soon, however, as there is a slight excess of silver ions, these are adsorbed on the silver bromide formed, together with eosin, and give the precipitate a brick-red colour. The indicator is extremely useful for dilute solutions, and will give accurate results with concentrations down to $M/1,000$. Fluorescein is also used in the determination of chlorides by means of silver nitrate. It is important to remember that it is not the colour of the solution which changes, but that of the precipitate. Other dyes which will act as adsorption indicators in silver titrations, and some other precipitation titrations are, dichlorofluorescein, di-iodofluorescein, and other fluorescein derivatives, Biebrich scarlet, pheno-safranine, tartrazine, and rhodamine 6 G.

367. Chromatography.—Substances can be selectively adsorbed from solution, and an application of this fact is now widely used in analysis for carrying out separations which would involve very lengthy and difficult procedures by ordinary chemical methods. Because the method was first used by the Polish botanist Tswett (1906) to separate the carotenes, which are plant pigments, and coloured adsorption complexes are formed, the process is called chromatographic analysis. Although it was used by Tswett as early as 1906, it was not until 1930 that the value of the method came to be recognised, and it became a common laboratory technique.

If a solution of plant pigments, such, for example, as the extract obtained by boiling leaves with acetone, is allowed to flow through a long tube packed with an adsorbent, such as alumina, the different pigments are adsorbed at different stages of their journey down the tube. The most easily adsorbed substances will collect at the top, the less readily adsorbed will pass further down before they are removed.

Coloured bands are therefore seen in the column of adsorbent. This is called a chromatogram. The initial separation is sometimes not very distinct, and can be improved by passing some of the pure solvent through the column. This is called the development of the chromatogram; what happens is that some of the less readily adsorbed substances are redissolved and adsorbed again further down the tube, thus spreading out the coloured zones. In this way it is possible to obtain an almost complete separation of a complex mixture.

The adsorbents commonly employed are alumina (specially prepared for the purpose), magnesium oxide, and sucrose. The solvents are usually organic—acetone, benzene, and petroleum ether being frequently used.

When the chromatogram has been obtained, the column of adsorbent can be pushed out of the tube and cut into sections at the various zone boundaries. The adsorbed substance can then be dissolved out with a suitable solvent. This process is called elution. Another method is to pour more of the solvent through the column and collect each component as it reaches the bottom of the tube.

For colourless substances various methods can be used. They may be converted into coloured compounds, and then decomposed again when the separation has been effected. Some colourless compounds give a fluorescence when exposed to ultra-violet light, and this method has been used to detect the zone boundaries.

Chromatographic analysis has proved to be a very valuable method and has been used not only for the separation of complex mixtures, but for the purification of substances, the detection of impurities, the concentration of dilute solutions of naturally occurring organic compounds, and a number of other purposes.

368. Partition Chromatography.—The chromatographic methods outlined above depend on the differential adsorption of components on an adsorbing column. Martin and Synge in 1941 developed another method of chromatographic separation which depends on the differences of partition of substances between different solvents. In the original experiments of Martin and Synge a small quantity of a solution of a mixture of acetylated amino acids was placed on a silica gel column. This gel contains a large quantity of water; we can regard it as water on a silica support. A solvent which is not fully miscible with water is allowed to travel down the silica gel. The solvent used originally was chloroform mixed with a little butanol. The solvent as it moves along carries the different acetylated amino acids at different rates along the gel. This difference in rates is due to the differences of the partitions of the various acids between water and the chloroform-butanol mixture. In this example water is what is called the stationary phase; the organic solvents are a mobile phase. The function of the silica gel is to act as a support for the solvents. It has since been found con-

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venient to use cellulose in the form of filter paper as a stationary phase support.

Paper chromatography may be carried out experimentally in a number of ways. For example a drop of a solution of a mixture is applied to one end of a strip of filter paper. The paper contains water which is in equilibrium with the water vapour of the atmosphere. The strip is placed vertically in a vessel with the end at which the solution has been applied dipping into a container which contains the solvent which is to act as the mobile phase. This can be arranged so that the solvent can either travel up or down the paper: that is the test spot may either be at the bottom or the top of the strip of paper. The whole apparatus is enclosed in a jar to ensure constancy of atmospheric conditions. The atmosphere in this jar should be saturated with the vapour of the solvents which constitute the mobile and the stationary phases. The mobile solvent will move along the paper until it reaches the test spot; it then carries the various components present in the test solution at different rates. The strip is left for some hours while this process continues. It is then removed from the container, dried, and the distances which the various components have moved are observed. The components will appear as a number of coloured spots at different distances along the paper. If the substances present are colourless then the positions on the strip may be detected by spraying the paper with a solution which contains a reagent capable of reacting with the various substances present to give coloured compounds. For example ninhydrin is used when mixtures of amino acids are being separated. Alternatively if the components fluoresce in ultraviolet light then their position in the strip may be detected by exposing the paper to ultraviolet light and noting the points at which fluorescences appear.

The distance which the mobile phase has moved along the paper can also be measured. The ratio of the distance a component has moved to the distance the solvent has moved is called the R_F value. This is characteristic for each component in a mixture. The R_F value for any component will be changed if the partition is carried out between a different set of solvents.

While the difference in partition of components between solvents is the primary reason why the components are separated in partition chromatography it may be pointed out that adsorption on the support also occurs. Apart from cellulose and silica gel, powdered rubber, starch, Celite and kieselguhr have been used as stationary phase supports in separations involving organic materials. Cellulose has been used almost entirely for separations of inorganic substances. It is not necessary that water should be the stationary phase. Non-aqueous systems may also be used. It is only necessary that the solvents used in the stationary and mobile phase should not be completely miscible.

One most important aspect of partition chromatography is that it enables separations to be carried out when only very small quantities (of the order of milligrams) of material are available. The outline given above of partition chromatography is necessarily brief. For fuller accounts the reader is referred to articles by Martin in *Endeavour* (1947, p. 21) and the *Annual Reports on the Progress of Chemistry* (1948, p. 268), and Williams in *Research* (1948, Vol. I, p. 400). A recent survey of inorganic chromatography is given by Wells in the *Quarterly Reviews of the Chemical Society* (1953, p. 307).

369. Surface Films.—It follows from the Gibbs Absorption Law that the surface layer of solutions of a surface active compound, has a greater concentration of solute than has the bulk of the solution. As we ascend the homologous series of fatty acids this effect becomes more pronounced. Also the solubility of the acids decreases. When the acids contain about eleven carbon atoms their solubility becomes negligible and they form an insoluble film on the surface of water. Surface films demonstrate in two dimensions the properties that bulk matter shows in three. The surface films are made up of a layer of molecules one molecule thick. The molecules are oriented with the carboxyl groups pointing into the water and the hydrocarbon chains pointing outwards from the water. Surface films are studied in the Langmuir trough (see Fig. 220). This consists of a shallow rectangular

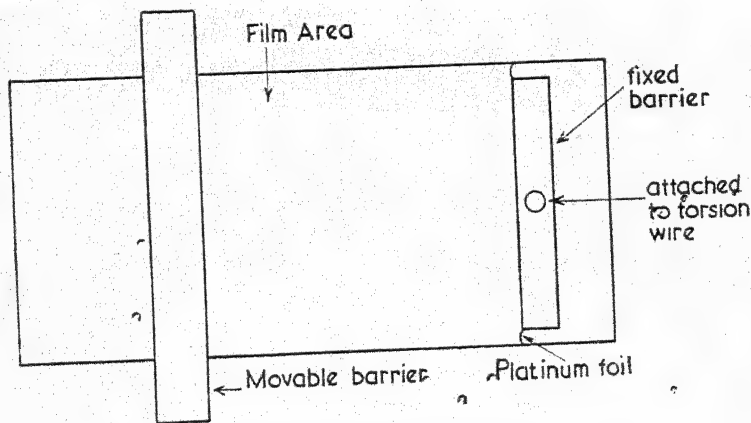


FIG. 220.—Langmuir Trough.

trough filled to the brim with water. The film is held on the surface between two barriers. These can be strips of waxed paper or glass which lie across the surface of the water. One barrier is fixed and is attached to a torsion wire arrangement by which the force exerted by the film is measured. Small pieces of platinum foil are placed between the ends of the barrier and the sides of the trough to prevent the film moving

round the sides of the barrier. The second barrier, which is supported by the sides of the trough is movable, so the area of surface between the barriers can be varied. The compound under examination is dissolved in a volatile solvent and a known quantity of this solution is dropped on to the surface of the water between the fixed and movable barriers. The solvent evaporates leaving the compound which forms a film.

The variation of the force exerted by the film (measured by means of the torsion wire) with the area of the film (varied by means of the movable barrier) can now be studied. A plot of such a force-area curve can be made and a typical curve is shown in Fig. 221. The first portion

of the curve AB corresponds to a small force exerted by the film. In the part of the curve B to C it can be seen that a very small decrease in film area leads to a very large increase in the force exerted by the film; the molecules at this stage are tightly packed together and resist strongly any attempt to compress them further; finally at C the film collapses and the molecules in the monolayer start to pile on top of one another. Extrapolation of the line CB to D gives us the area occupied by the film when the molecules are closely packed together. Knowing the weight of compound in the film (w) and the molecular weight (M) of the compound forming the film and the Avogadro number N_0 we can calculate the number of molecules in the

film; this is $N_0 \frac{w}{M}$. Dividing this into the

area D we can calculate the area each molecule occupies on the film. This works out to be about 20.5 sq. A. for the fatty acid series. The fact that this area is the same for the various members of the series shows that the acids are packed pointing perpendicularly to the surface. The same area per molecule is found for films of long chain amides, alcohols, methyl ketones and other substances containing a long hydrocarbon chain attached to a polar group. The figure 20.5 gives the area of cross section of the hydrocarbon chain. The consistency of the results indicates that the view that the hydrocarbon chain of the molecules is vertical to the surface with the polar group in the water is correct. X-ray results give a value for the area of cross section of a hydrocarbon chain which agrees with that obtained from surface film measurements. If more molecules of the compound are spread than are necessary for the formation of a monomolecular layer on the area available for the film, the excess molecules do not spread on the mono-

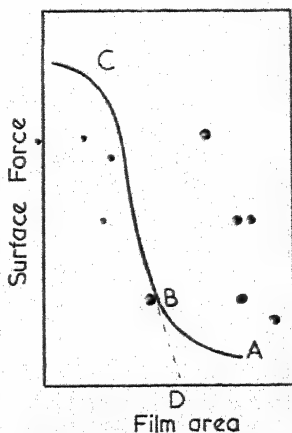


FIG. 221.—Curve of surface force against area for a surface film.

layer, but remain as a lens localised in one portion of the surface.

370. Emulsions.—A colloidal system involving one liquid dispersed in another is known as an emulsion. For example oil can be dispersed in water to form what is called an oil in water emulsion; in contrast water can be dispersed in oil to form a water in oil emulsion. The dispersed particles in an emulsion are about $\cdot 1$ to 1μ in size. The formation of an emulsion will lead to a large increase in the interfacial area between the components forming the emulsion. Because of this, emulsions formed from just one component dispersed in another are not very stable. To be stable an emulsion requires the presence of a third substance known as an emulsifying agent. These agents reduce the interfacial tension between the two components forming the emulsion. Among the many emulsifying agents are soaps and detergents. These compounds have long hydrocarbon chains attached to a polar group. At an oil-water interface the hydrocarbon chain is absorbed on the oil side of the interface; the polar group on the aqueous side.

Detergent action is related to the stabilisation of an emulsion. If we consider the action of a detergent solution on a grease layer on fibre, three stages in the cleansing of the fibre may be distinguished. The detergent is more strongly adsorbed at the fibre water interface than the grease, and so displaces the grease layer. As the latter is displaced it is rolled into a globule. The globule is detached from the fibre into the water and is then emulsified with the detergent acting as an emulsifying agent.

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CHAPTER XVIII

CATALYSIS

371. Development of the Theory of Catalysis.—A broad definition of catalysis is "the acceleration or retardation of chemical reactions by the addition of small quantities of foreign substances to the reacting system".

It is remarkable that catalysis, which to-day plays such an important part in every branch of chemistry, including particularly the technical side of the subject, was very little investigated before 1800. Like many other branches of chemistry, its study was facilitated by the atomic theory of Dalton, and the development of stoichiometry. The use of certain catalysts, however, goes back a long time before 1800, though there was no theory of their action. Particularly, the process of fermentation has been known for centuries. The action of yeast was one of the earliest phenomena to interest men of science. The "Philosopher's Stone" and the "Elixir of Life" may both be regarded as catalysts, long sought after, but never reached. The idea of gold acting as a "ferment", a small portion engendering a much greater quantity, long precedes the Philosopher's Stone. It is found in the work of Zosimus (*ca.* A.D. 300) if not in earlier writers. One of the early references to catalysts in alchemy is given by Löwenstern in his book "Laboratorium Chymicum", the fourth edition of which was published in 1767. He refers to an alchemist, Schwerzer, who, in the year 1585, had produced an "elixir" of which "one part would tinge 1024 parts of base substances". There is, however, a long distance between this and the first definite observations of catalysis in which a catalyst was shown to be able to accelerate chemical reactions without any violation of the stoichiometrical laws.

The first catalytic reactions which were studied at all systematically were (a) the conversion of sulphurous acid into sulphuric acid, forming the basis of the lead chamber process for the manufacture of this acid; this was known in the eighteenth century; (b) the hydrolysis of an aqueous solution of starch by acids to give sugars (Parmentier, 1761, Kirchoff, 1811); (c) the catalytic decomposition of hydrogen peroxide by metals (Thenard, 1818); (d) the oxidation of combustible vapours by air in the presence of a heated platinum wire (Davy, 1817), or platinum sponge (Döbereiner, 1823). This discovery caused a great sensation, and really started the investigation of heterogeneous catalysis.

Later in the nineteenth century a large number of other catalytic

reactions were discovered and investigated. Of the characteristics of catalytic action which were thus demonstrated, the one that stands out above all the rest is the fact that the catalyst is not used up in the process. Relatively large quantities of the reacting substances could be brought into reaction by the use of a small quantity of catalyst, and there appeared to be no reason why, if the presence of impurities or the possibility of mechanical loss were avoided, an unlimited quantity of the reactants could not be transformed by a finite quantity of the catalyst, however small. Further, it was found that catalytic action was specific, not every catalyst being able to bring about every reaction. A catalyst frequently could only be chosen after numerous experiments. It was also discovered that a catalyst could be rendered inactive by the presence of certain substances. This was first shown by Döbereiner and Faraday.

The name "catalyst" was first given to these active substances by Berzelius in 1835. It is to be noted that quite thirty years passed, after catalytic changes were studied thoroughly, before the phenomenon was given a name.

It was soon recognised that catalysis could fall into two, or possibly three, classes. The first is homogeneous catalysis, where the catalyst is in the same phase as the reactants. One of the earliest of catalytic reactions, the lead-chamber process of making sulphuric acid, belonged to this class. The second is heterogeneous catalysis, in which the catalyst is in another phase from the reactants. This is the more important of the two classes, and is represented in the early work by Döbereiner's experiment with combustible gases and oxygen. The third need not be classed as a new type, but it is convenient to do so. It comprises the biological catalytic processes, of which the reactions due to enzymes were very early known. The hydrolysis of starch by means of diastase from germinating barley was investigated by Irvin in 1785, and by Kirchhoff in 1814. Another early example was the breakdown of amygdalin by emulsin, studied by Liebig and Wöhler in 1837.

Theories as to the cause of catalysis were not long in following the observations. In the first decade of the last century these explanations centred round thermal effects of some kind, such as local heating, or certain electrical effects. These were discarded by Döbereiner and Davy and others. A very important work on the action of nitric oxide in the lead chamber process was published by Clement and Désormes in 1806, in which they pointed out that the nitric oxide acted as a carrier of oxygen owing to the formation of an intermediate compound, NO_2 . This explanation, which is still regarded as correct, made others think that all catalytic action was possibly due to the formation of intermediate compounds, with the result that, in order to explain these reactions, all sorts of chemical compounds which could have no possible chance of existence were postulated. Faraday, however, did not agree

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with the formulation of compounds which had no separate existence, and which violated the ordinary chemical laws, and, being particularly concerned with the action of platinum in bringing about the combustion of a mixture of hydrogen and oxygen, proposed the adsorption theory. These two views, those of the formation of intermediate compounds and of adsorption, have held the field with few modifications ever since. It is interesting to note that the modern theory of adsorption which postulates the existence of special points on surfaces at which adsorption takes place, was anticipated to a certain extent by Schweigger in 1823, who refers to the existence on the surfaces of solid bodies of "anlagenspunkter", at which catalysis commences.

The various theories of catalysis will be dealt with more fully later, but it may be said that during the nineteenth century the knowledge of the phenomenon of adsorption was so scanty that the intermediate compound theory was almost universally acknowledged to be correct, although some, such as Mercer and Playfair, looked at the question from the point of view of affinity. Mercer—known for his discovery of "mercerisation"—stated in 1842 that catalysts were substances with weak chemical affinities, so that if intermediate compounds were formed they would of necessity be rather unstable. Playfair, in 1848, extended this view, and stated that catalysts possessed additional affinity, which was added to the affinity of the reactants, and thus caused the reaction to go faster. The intermediate compound theory received further enhancement by the discovery in 1867 by Deacon of his process for the manufacture of chlorine from hydrogen chloride by passing it over heated cupric chloride in the presence of oxygen. He was actually seeking examples of catalysis involving intermediate compound formation when he came across the formation of chlorine by heating cupric chloride in air, and combined this with the regeneration of cupric chloride by heating cuprous chloride with hydrogen chloride and air.

Schönbein, in 1850, stated that no chemical reaction, whether catalytic or not, must be regarded as taking place directly according to the equation, but that each chemical process is made up of a series of elementary processes. This was a further aid to the intermediate compound theory. The introduction of a new substance into the system in the form of a catalyst meant the possibility of new elementary processes. The theory would also explain the specific nature of catalysts, and also the poisoning of catalysts (§ 376).

The whole study of catalysis was put on a new footing by the work of Ostwald. In 1888 he formulated a series of criteria of catalysis, which summed up the behaviour of catalysts. These points are:

(1) *The catalyst remains unchanged at the end of the reaction.*—This only applies to the chemical composition of the catalyst. Its physical form may change completely. Thus, if coarsely powdered manganese

dioxide is mixed with potassium chlorate in the preparation of oxygen, at the end of the reaction it is found to be finely powdered.

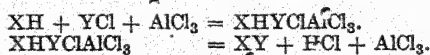
(2) *A small amount only of catalyst is required.*—This is not invariably true. Many examples are known where the catalyst must attain a definite minimum concentration before it will act. An example of this is provided by the Friedel and Crafts reaction in organic chemistry, where aluminium chloride is used to promote the reaction between an aromatic hydrocarbon, such as benzene, and an aliphatic halide, such as ethyl chloride. Here, however, it is known quite definitely that an intermediate compound is formed.¹ On the other hand, it is known that in many cases a very small amount of catalyst is sufficient for the purpose. Attempts have been made to determine the threshold concentration of catalyst required, but they have not been very satisfactory.

(3) *A catalyst alters the speed of the action, without, however, altering the final state of equilibrium.*—This is true where the catalyst is needed only in small concentration, and indeed this criterion would be required from the application of the law of conservation of energy. If, however, the catalyst is present in large quantity, there is no need for this to be true, and experiments carried out by Jones and Lapworth on the equilibrium constant of the hydrolysis of ethyl acetate in the presence of varying amounts of hydrochloric acid, which acts as a catalyst, indicate that it is not true when the amount of acid used is large.

(4) *A catalyst cannot start a reaction, but only increases or decreases its speed.*—This, again, is probably not true. Many reactions are known to be initiated by a catalyst. Of course, there is always the reply to this objection that the reaction may proceed so slowly without the catalyst that its speed cannot be measured.

372. Heterogeneous Catalysis.—This class of catalysis includes the majority of these reactions which are of commercial importance, and has been studied therefore to a much greater extent than homogeneous catalysis. In this type, the catalyst is a separate phase from the reactants, which are usually gases. The catalysts that have proved most useful in this field are the metals platinum, nickel, copper and iron, usually in a state of fine division, and certain metallic oxides, chiefly those of iron, zinc, chromium, bismuth and molybdenum. This is not, of course, an exhaustive list.

¹ The explanation of the Friedel and Crafts reaction is expressed by the equations:—



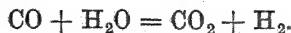
It is necessary to add at least one gram-molecule of aluminium chloride to each gram-molecule of the reacting substance. It is extremely probable that the aluminium chloride is not a catalyst at all, but that the co-ordination compound formed ($\text{XHYCl} \cdot \text{AlCl}_3$) is immediately decomposed. To return to the original theory, Böeseken has supposed that a large excess of the catalyst is required, as some is used up in the formation of the co-ordination compound, and more must be added to provide some of the free catalyst.

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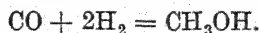
Catalysts are usually specific in their action. One catalyst may serve for an hydrogenation, whilst it would be useless for an oxidation.

Important technical processes using the phenomenon of heterogeneous catalysis are:—

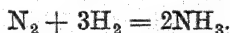
(1) The preparation of hydrogen from water gas and coke oven gas. The carbon monoxide of the water gas is converted into carbon dioxide by the action of steam in the presence of ferric oxide to which a promoter (§ 375) has been added.



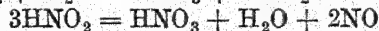
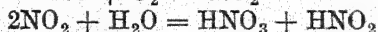
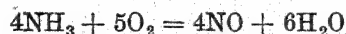
(2) The preparation of methyl alcohol from carbon monoxide and hydrogen, using as a catalyst zinc oxide together with chromium oxide as a promoter.



(3) The Haber process for synthesising ammonia in which nitrogen and hydrogen in the correct proportions are passed over a heated catalyst, formerly platinum, but now mainly iron, containing a promoter.

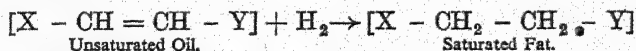


(4) The oxidation of ammonia to form nitric oxide, and, ultimately, nitric acid.



The catalyst formerly employed was platinum wire gauze, but now the cheaper mixture of ferric and bismuth oxides has taken its place.

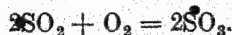
(5) Hydrogenations, such as the conversion of liquid oils into solid fats, as in the manufacture of margarine. The catalyst is finely divided nickel.



Unsaturated Oil.

Saturated Fat.

(6) The contact process for manufacturing sulphuric acid. Sulphur dioxide is directly oxidised by atmospheric oxygen in the presence of platinum.



(7) The removal of sulphur compounds from coal gas. Hydrogen sulphide is removed by passing the gas over ferric oxide in the presence of sawdust.



The other volatile sulphur compounds in the gas are converted into

hydrogen sulphide by passing over a hydrogenation catalyst, *e.g.*, metallic nickel. The hydrogen sulphide is then removed as above.

(8) The use of activated charcoal. This charcoal is prepared from special woods, and is largely used in chlorinations. The liquid to be chlorinated is passed down a tower filled with activated charcoal, whilst the chlorine gas is passed up. Hydrogen chloride is now manufactured by passing a mixture of hydrogen and chlorine over activated charcoal.

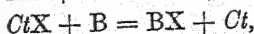
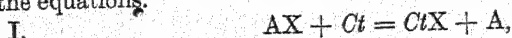
Further details of these reactions will be found in text-books of Inorganic Chemistry.

373. Enzyme Catalysis.—Enzymes probably act in solution, and therefore may be homogeneous catalysts. They are complex organic compounds, which are not very stable, and form colloidal solutions with water. They catalyse numerous reactions, especially those connected with natural processes. Most of them are hydrolytic in their action, *i.e.*, they cause the addition of water to a substance. Thus, diastase converts starch into maltose, and maltase, a different enzyme, will cause the hydrolysis of maltose into glucose. Invertase converts sucrose into a mixture of glucose and fructose; and zymase converts glucose into alcohol.

The exact mechanism of the working of enzymes is not known, but they are extraordinarily important substances in the human body.

374. Mechanism of Catalysis.—It has already been stated that there are two broad theories of catalytic action, one of which may be termed the "chemical" theory, and the other the "physical" theory. The first postulates the formation of intermediate compounds, often of doubtful composition, whilst the latter supposes that adsorption takes place. These two views have now been brought into harmony by the work of the last twenty years.

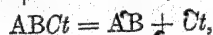
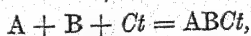
The Intermediate Compound Theory.—Intermediate compound formation may result in reactions of two types, which may be represented by the equations:



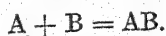
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II.



giving

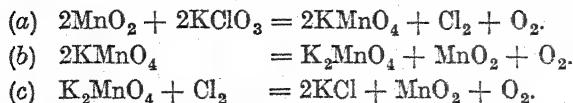


In these equations the symbol *Ct* stands for the catalyst.

There can be no doubt that in a very large number of cases of catalysis intermediate compounds are formed. One need only quote the lead chamber process for the manufacture of sulphuric acid, which is usually regarded as a catalytic process, to show that here intermediate compound formation is necessary. Actually this is a case of homogeneous catalysis, as both the catalyst and the reactants are in the

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same phase, *viz.*, the gaseous phase. The production of oxygen by heating a mixture of manganese dioxide and potassium chlorate is another reaction in which intermediate compound formation is probable. This reaction has been regarded by McLeod as consisting of the following successive changes:

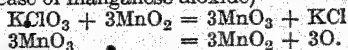


This accounts for the fact that in this reaction the oxygen is often contaminated by a small quantity of chlorine, and that the residue, if a small quantity of manganese dioxide only is used, is often coloured pink.¹ There have been physical explanations of this reaction, one of which was that on heating the potassium chlorate a supersaturated solution of oxygen in potassium chlorate is obtained, which is broken up when manganese dioxide is added, just as when dust particles enter a supersaturated solution of a salt. If this is true, then any fine powder should bring about the decomposition. It is a fact that some other powders do so, but it is certainly not a general phenomenon. Also, when the pressure is reduced over ordinary potassium chlorate, it does not facilitate the decomposition as it would be expected to do if the salt were a supersaturated solution.

The very fact that intermediate compound formation can take place in catalytic reactions indicates that the stability of such compounds must be small. Otherwise they would not undergo change in such a facile way. This may account for the fact that they frequently cannot be isolated. On the other hand, there are many reactions in which the presence of these compounds is ruled out on grounds of stoichiometry, and to these the adsorption theory may be applied.

The *adsorption theory* states that before reaction the reactants are adsorbed on the surface of the catalyst. The origin of this idea may be traced to Faraday. There is no definite chemical compound, but an "adsorption compound" of no definite composition, possibly one molecule thick, is formed at the surface. The work of Hardy, Langmuir, Adams and others on the nature of thin films has added enormously to our knowledge of adsorption. Also, our modern knowledge about the electrical structure of the atom, and the nature of chemical combination,

¹ McLeod's theory cannot be reconciled with the fact that nickel oxide, NiO, and ferric oxide, Fe₂O₃, are *quantitatively* as good catalysts in this reaction as manganese dioxide. CuO does not catalyse the reaction. These facts suggest that the reaction may be (in the case of manganese dioxide)



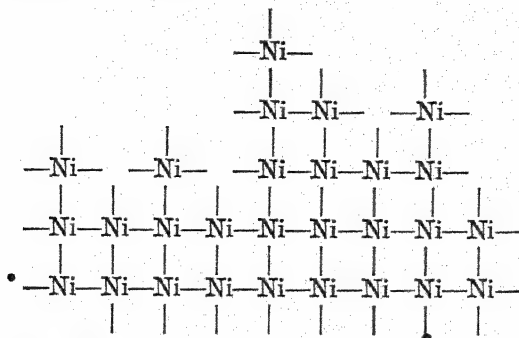
MnO₃ has not, however, been isolated from this reaction. NiO might form a higher oxide in a similar manner. CuO could not, as no higher oxide of copper is known. McLeod's theory fails with NiO, as this substance, although a better catalyst than manganese dioxide, could not form a nickelate.

makes it obvious that there is no essential difference between physical and chemical forces. The same forces which can hold the molecules or atoms of the catalyst together can act at its surface to attract molecules of other substances and give rise to adsorption. This explains very well the fact that the more finely divided the catalyst is, the better does it work. There will be greater surface and more room for adsorption to take place. For reaction to occur the two molecules which are going to react must presumably be adsorbed side by side; the new molecule is then formed and evaporates off, leaving the space clear for the next molecules to be adsorbed, and so on.

The increase in concentration which must occur in the adsorbed phase would alone account in some measure, though not completely, for acceleration of reaction. Also, the surface of a solid is often capable of taking up the energy liberated in the reaction (heat of reaction), and this may perhaps be used in enhancing chemical reactivity throughout the mass of reacting substances. If, for example, two bromine atoms collide in the gaseous phase and form a molecule, the heat of reaction, 46,000 gm.-cals. per gram-molecule, is carried momentarily by the bromine molecule. This amount of energy is comparable with the heat of dissociation, so that the newly formed molecule will be very likely to decompose again unless this energy is given up. The presence of a third body, taking no actual part in the reaction, would help to remove this energy. The chance for a triple collision occurring in the gas phase is small, but when there is a solid surface present everywhere, the chance is much greater. It is recognised that this theory cannot be of universal applicability, since any surface ought to be capable of acting in this way.

Langmuir's ideas on adsorption may be applied to catalysis. A monolayer of gas atoms is adsorbed on the surface of a catalyst. The molecules of reacting gases are adsorbed at different points on the surface. They then react to form their products which are desorbed from the surface into the gas phase. It can be shown that the energy necessary to bring about a gas reaction is lessened by the presence of an adsorbing surface. It is possible that when a gas molecule is adsorbed, bonds in other parts of the adsorbed molecule are loosened, thus helping the progress of the reaction. As pointed out previously adsorption at the surface of a solid may be of two types, van der Waals and chemisorption. When the latter occurs in the course of a chemical reaction the intermediate compound theory and adsorption theory both find a place in our explanation.

It is also known that catalytic activity is not uniformly distributed over the surface of a catalyst. There appear to be active spots. Catalysts have been examined by X-ray methods and shown to possess a crystalline structure, but on the surface the catalyst will be uneven. If we represent the surface of a nickel catalyst as follows:—



The lines represent the chemical forces acting between the atoms, and do not stand for valency bonds. It is obvious that at the peaks there will be a greater number of unsatisfied forces, which can be used to attach molecules. Isolated nickel atoms would be centres of great activity. Boundaries between crystals, and cracks and imperfections—indeed discontinuities in general—probably act as active centres. This explains the fact that the activity of a catalyst depends a good deal on its method of preparation and is enhanced when the surface is increased. Hence the great catalytic activity of such substances as platinum black.

The mechanisms of the reactions on surfaces is still not clear. The catalytic hydrogenation of ethylene has been extensively studied: even for this reaction at least three mechanisms have been proposed. One mechanism involves the chemisorption of both ethylene and hydrogen atoms: the ethylene is then supposed to react successively with the hydrogen atoms. Another mechanism suggests that only the hydrogen or the ethylene is chemisorbed. The third mechanism envisages the adsorption of ethylene as an acetylenic type of compound. None of these mechanisms has been definitely proved correct. This reaction shows the complicated nature of the problems involved.

375. Promoters.—The activity of a catalyst is frequently enhanced by mixing it with some other substance, not necessarily itself a catalyst. This action is called "promoter" action. Thus, in the Haber process for the synthesis of ammonia, it has been found that mixed catalysts of the composition $\text{Fe} + \text{Al}_2\text{O}_3 + \text{K}_2\text{O}$ are particularly active; in the oxidation of ammonia, iron oxide and bismuth oxide may be used; and the synthesis of methyl alcohol from carbon monoxide and hydrogen is well catalysed by zinc oxide mixed with chromium oxide or other oxides as promoters. No definite theory can be put forward concerning these facts. Possibly the effect of the promoter is to increase the number of active spots by increasing the number of discontinuities in the crystal.

376. Poisoning of Catalysts.—Very frequently the presence of small quantities of impurities in the reacting substances will render the

catalyst useless. These are called "catalyst poisons". It is a remarkable fact that substances which poison catalysts are usually also poisonous to organisms. Thus arsenious oxide and hydrogen cyanide are two of the most powerful of catalyst poisons. The poison may be specific. The amounts of various poisons necessary to reduce the velocity of decomposition of hydrogen peroxide to one-half of its original value have been determined, when the reaction has been catalysed by colloidal platinum and by hæmase (an enzyme present in blood). The results are embodied in the Table below.

TABLE CIII.—CONCENTRATION OF POISON REQUIRED TO REDUCE THE RATE OF DECOMPOSITION OF HYDROGEN PEROXIDE TO ONE-HALF

Poison.	Catalyst. Concns. in gm.-mols./litre.	
	Colloidal Pt.	Hæmase.
Hydrogen cyanide	5×10^{-6}	1×10^{-6}
Mercuric chloride	5×10^{-7}	5×10^{-7}
Hydrogen sulphide	3×10^{-6}	1×10^{-6}
Carbon monoxide	very poisonous	no poisoning
Aniline	2×10^{-4}	2.5×10^{-3}
Hydrogen chloride	3×10^{-4}	1×10^{-5}
Iodine in potassium iodide	2×10^{-7}	2×10^{-5}

It is seen that the poisons do not affect the two catalysts in the same degree. It is clearly very necessary to prevent poisoning of catalysts on the technical scale.

The effect of poisoning is probably a reduction of the number of active spots. All the poisons are very highly adsorbed (a fact which also explains, in part, their poisonous action to the human body), and will therefore quickly cover the active centres and render the catalyst useless. The poisoning is not always permanent. If the poison is held only on the surface by adsorbing forces, it may be removed again if circumstances are favourable. On the other hand, poisons frequently form chemical compounds with the catalyst. Particularly is this so with hydrogen sulphide and the metal catalysts.

The poisoning of catalysts is not altogether an evil, and may sometimes be useful. In organic reactions it is sometimes necessary to stop the reaction at a certain stage, and this can be done by addition of a certain amount of a specific poison which will prevent the catalyst from reacting past a certain point.

Reactions can frequently be slowed down by the addition of some foreign substance, which is then sometimes referred to as a *negative*

catalyst. For example the oxidation of benzaldehyde by oxygen gas is stopped by a small quantity of hydroquinone. It has been suggested that the negative catalyst is absorbed on the wall of the reaction vessel and that as oxidation is a wall reaction the effect of the hydroquinone is to poison the wall which would serve as an oxidation catalyst. This view is incorrect. The oxidation of benzaldehyde is a chain reaction and hydroquinone acts as a chain breaker. Thus the function of a negative catalyst is to act as a chain breaker.

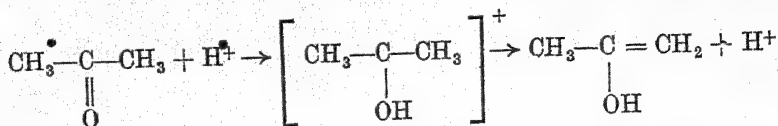
377. Autocatalysis.—Frequently in the course of a reaction a substance is formed which catalyses the reaction. This phenomenon is called "autocatalysis". An example is found in the titration of oxalic acid by means of permanganate. When the first portion of permanganate is added to warm oxalic acid solution, there is an appreciable period before it is decolorised. The second portion is, however, decolorised immediately. This is because manganous salts catalyse the reaction. They are formed when the first portion of permanganate has been used up, and the succeeding portions are therefore decolorised more rapidly.

A more striking example is found in the formation of chloric acid from potassium chlorate by adding sodium bisulphite solution. The weakly acid bisulphite liberates some chloric acid, which is an oxidising agent, and oxidises the bisulphite to the more strongly acid sodium bisulphate. This is then capable of liberating more chloric acid, and so the reaction proceeds until the whole mass froths up.

378. Homogenous Catalysis.—We consider here the catalytic action of hydrogen and hydroxyl ions. Hydrogen ions catalyse reactions such as the hydrolysis of esters and the inversion of sucrose. The velocity of these reactions is directly proportional to the concentration of hydrogen ion present. Hydroxyl ions have a similar catalytic effect, in reactions such as the mutarotation of glucose. It was first assumed that the hydrogen ion was the effective catalyst but Arrhenius showed that the addition of neutral salt had the effect of increasing the catalytic activity. This was observed whether the salt had or had not an ion in common with the acid used. It has since been shown that not only hydrogen and hydroxyl ions but also undissociated acids and bases and even cations of weak bases and anions of weak acids can have catalytic activity. It is often found that when one acid catalyses a reaction all acids in the widest sense catalyse that reaction. This is called general acid catalysis. General base catalysis refers to catalysis by bases. The influence of the hydroxyl ion is usually greater than that of the other basic catalytic species.

Some reactions are catalysed by both acids and bases. The term specific catalysis refers to certain reactions such as the hydrolysis of acetal in which the catalytic effect of hydrogen ion is very much greater than that of any other ion.

Acid catalysis results from the tendency of an acid to lose a proton; base catalysis from the tendency of a base to gain a proton. In considering the mechanism of acid or base catalysed reactions the losing or gaining of a proton by a catalyst must be involved in any suggested mechanism of the reaction. The iodination of acetone may be considered as an example. The acetone is supposed first to combine with hydrogen ions giving an enolic substance, which splits off a hydrogen ion and becomes the enolic form of acetone. This is unsaturated, and can obviously react very readily with iodine.



It is clear that what is wanted to catalyse this reaction is something that can supply and remove hydrogen ions, *i.e.*, an acid and a base. In aqueous solutions of acids it is thought that the water acts as the necessary base.

This view is also supported by the work of Lowry on the mutarotation of glucose in non-aqueous solutions. α -glucose itself is insoluble in organic liquids, and so tetramethyl glucose was used instead. In pyridine, a base, or in cresol, an acid, the rate of mutarotation was very much less than in water, but in a mixture of the two solvents the mutarotation was much greater than in water. Obviously, then, both base and acid were needed.

There are two explanations to account for the effect of an added salt on catalytic activity. One is that the salt may change the concentration of catalytically effective ions: the other that the salt increases the concentration of the electrolyte taking part in the reaction.

SUGGESTIONS FOR FURTHER READING

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CHAPTER XIX

PHOTOCHEMISTRY

379. The Absorption of Light.—Photochemistry is concerned with reactions which are accompanied by the absorption or emission of light, the term "light" being used in its widest sense to include all radiation.

When light falls on any body, part of it is reflected, part may be transmitted, and part may be absorbed. The principles of energy demand that *only the absorbed light should be effective in bringing about chemical action*. This was established by Grotthus on theoretical grounds in 1818, and confirmed by Draper in 1839 by experiment. It is usually called the *Grotthus-Draper Law*. The converse of the Law is not true. All absorbed light does not bring about chemical action. In many cases light is absorbed without any apparent chemical effect. Thus light is strongly absorbed by solutions of potassium permanganate over certain spectral ranges, but no chemical effect is noticed. The energy thus absorbed is converted mainly into thermal energy. We shall also discover later that the light causing a reaction need not be absorbed by the substance itself, but by another in the vicinity of the substance which undergoes change, the absorbing body being itself chemically unaffected. This occurs in the phenomenon known as sensitisation (§ 390).

380. Fresnel's Reflection Law.—It was shown by the physicist Fresnel, that the proportion of the incident monochromatic light reflected by a surface perpendicular to the incident beam is given by

$$I_r = \left(\frac{n - 1}{n + 1} \right)^2 I_i = KI_i,$$

where I_r and I_i are the intensities of the reflected and incident light respectively, and n is the refractive index of the reflecting medium for light of the wavelength used. Since n is a constant for constant wavelength and medium, the fraction $\left(\frac{n - 1}{n + 1} \right)^2$ may be written as a constant, K .

The amount of light which penetrates into the medium must be $I_i - I_r$. Not all of this passes right through. Some is absorbed, and only a fraction is therefore transmitted. The proportion of light absorbed is given by two laws, the first Lambert's Absorption Law and the second Beer's Law.

381. Lambert's Absorption Law.—Lambert, in 1760, found that layers of equal thickness of a homogeneous absorbing medium absorb equal proportions of the penetrating radiation. Consider a thin layer of the medium of thickness dx . If the light incident upon it is I_a , an amount of light dI_a will be absorbed, and according to the Law this is proportional to I_a .

$$\frac{dI_a}{dx} = -\kappa I_a.$$

On integration this gives

$$\log_e I_a = -\kappa x + c.$$

When $I_a = I_i$, $x = 0$.

$$\therefore c = \log_e I_i$$

$$\therefore I_a = I_i \cdot e^{-\kappa d}$$

where d is the thickness.

This is the mathematical expression of the Law. κ is called the "absorption coefficient". It is clear that the absorption depends on the number of molecules present. In layers of equal thickness there will be an equal number of molecules, which will absorb equal fractions of the light.

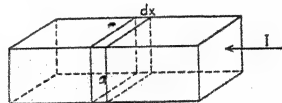


FIG. 222.

Bunsen, instead of using the absorption coefficient, used the extinction coefficient α , which is the reciprocal of that layer thickness, expressed in centimetres, at which I_i has fallen to one-tenth of its original value. It is an easy exercise to show that

$$\alpha = 0.4343\kappa.$$

382. Beer's Law.—This extension of Lambert's Law was put forward in 1852. The Law states that the degree of absorption of light depends on the thickness, d , of the layer traversed, and on the molecular concentration in that layer. Thus a layer of gaseous chlorine 20 cm. long at a pressure of 0.1 atmos. should possess the same transmission as a 10 cm. layer where the chlorine pressure is 0.2 atmos., a fact demonstrated experimentally by von Halban in 1922. The Law can be expressed mathematically in the form,

$$I_a = I_i e^{-k'cd}$$

or,

$$I_a = I_i \times 10^{-k'cd},$$

where

$$\alpha = 0.4343k'.$$

The constant k' is the molecular absorption coefficient, whilst α is the more frequently used molecular extinction coefficient. The latter is the thickness in centimetres of a layer of a molar solution which will reduce the intensity of light passing through it to one-tenth of its original value.

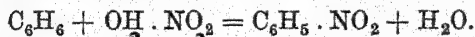
Beer's Law has a number of exceptions. It is usually found that at

high concentrations the substance absorbs more strongly than the equation requires.

The extinction coefficient, a , varies a great deal from substance to substance and also with the wavelength of the light used. If white light is allowed to fall upon a coloured transparent substance and the transmitted light is viewed through a spectroscope, it is found that the light is absorbed to a much greater extent in certain spectral ranges; so much so, in fact, that there is frequently practically no light transmitted at all at some wavelengths. These places of great absorption in the spectrum are called absorption bands, and are characteristic of the substances giving them. Absorption bands may also occur in the ultra-violet, and their study is of considerable importance in connection with the elucidation of atomic and molecular structure (§ 396).

The nature and position of the absorption bands decide the colour of the substance. A substance like chlorine absorbs chiefly in the blue and violet, and so the transmitted light (when white light is incident upon it) is a mixture of all the colours from green to red. Thus the substance appears yellowish-green. Bromine absorbs considerably more towards the red, and the vapour therefore possesses a brownish colour. Iodine absorbs strongly in the green, allowing violet and blue, and also the red end of the spectrum, to come through. Hence the vapour appears to be purple. Fluorine absorbs considerably in the ultra-violet and little in the visible, and therefore appears to us pale yellow in colour.

The absorption spectrum of a compound is closely related to its constitution, and, in fact, frequently provides useful information concerning it. The absorption spectra of tautomers are frequently different from each other. Hantzsch and others have used the method to investigate the tautomeric nature of certain organic substances. A good example of this is shown in the investigation of the constitution of nitric acid by von Halban. It is known that nitric acid will behave in two ways. When concentrated, it splits off an OH group and furnishes a nitro-group, NO_2 , for example, to a hydrocarbon of the aromatic series, such as benzene, which can provide an H atom to combine with the OH to form water.



Its constitution may here be represented as $\text{OH}(\text{NO}_2)$. In dilute aqueous solution, however, it splits off a hydrogen ion and forms salts with bases. Its structure must then be of the type $\text{H}(\text{NO}_3)$. Now nitric acid absorbs in the ultra-violet and the absorption bands have been measured for the concentrated and dilute solutions of the acid. The two sets of absorption bands are quite different from each other, and therefore indicate the existence of two different forms of the acid. As the concentrated acid is diluted, the absorption gradually changes from the

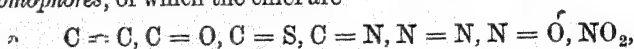
one form to the other, thus showing that there is a tautomeric equilibrium between the two forms of the acid at intermediate dilutions.

The investigation of the infra-red absorption spectra of substances is now used as a valuable method of analysis, particularly of organic compounds, such as hydrocarbon mixtures. This work has been largely developed by H. W. Thompson and his school. The infra-red absorption spectrum of nitric acid has indicated that the pure substance is associated and contains a hydroxyl group. The association may occur by hydrogen

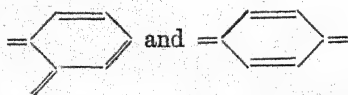
bonds between two molecules, *e.g.*,
$$\text{O} = \text{N} \begin{array}{c} \text{OH} \cdots \cdots \text{O} \\ \diagup \quad \diagdown \\ \text{O} \cdots \cdots \text{HO} \end{array} \text{N} = \text{O},$$

or in chains. When the acid is diluted, the intensity of the band due to the associated molecule rapidly diminishes and has almost disappeared at a concentration of 80 per cent.

The question of absorption spectra assumes great importance when dealing with the structures of organic colouring matters. The theory of the colour of organic compounds has yet to be worked out, but a few qualitative rules have been derived as the result of the work of Witt in 1876, and of Kauffmann in 1907. An organic coloured substance must contain one or more of a certain set of unsaturated groups, called *chromophores*, of which the chief are



and the *ortho*- and *para*-quinonoid structures



Compounds containing these only are usually lightly coloured. The introduction of other groups called *auxochromes* into the molecule intensifies the colour and shifts the absorption bands. Thus the introduction of OH, NH₂ or CH₃ moves the absorption bands towards the red. Others shift the absorption towards the blue, *e.g.*, CH₃CO—, and C₆H₅CO—.

The absorption spectrum of a substance may vary with the solvent. Some salts have their absorption spectra widely displaced on solution in different solvents. This may be due to solvation or deformation of the electron shells in various ways owing to the polarisation of the solvents used (§ 402).

383. Application of the Quantum Theory.—The laws so far mentioned do not depend for their truth on any hypothesis concerning the nature of light; but they do not lead very far, and as soon as we desire to find out the nature of a photochemical change the necessity of knowing more of the nature of the radiation producing it is apparent. According to the quantum theory, light is not a continuous radiation; it is made up of quanta of energy, the amount of energy in each quantum

being $h\nu$, where h is Planck's constant and ν the frequency of the radiation. Light cannot therefore be absorbed continuously, but only in multiples of this quantum. The number of quanta which will be absorbed by any given body will depend on the number of molecules which can absorb the light (i.e., to the product of c and d , where c is the concentration and d the thickness of the layer), and upon the probability that the molecules that can absorb will be in a condition to do so. The probability term corresponds to the molecular extinction coefficient α which, of course, varies greatly from substance to substance.

Clearly the greater the frequency of the light, i.e., the smaller the wavelength (for wavelength λ , and frequency ν , are connected by the equation $\nu = \nu\lambda$, where ν is the velocity), the greater will be the energy associated with the quantum. It is for this reason that ultra-violet light is specially active in bringing about photochemical changes. Table CIV gives (and Fig. 223 plots) amounts of energy associated with the quanta of radiations of various frequencies.

TABLE CIV.—ENERGY CORRESPONDING TO VARIOUS
WAVELENGTHS OF LIGHT

Colour.	Upper wavelength limit λ in Angstroms.	Energy per $h\nu$, ergs.	$U = Nh\nu$ gm.- cals.
Red . . .	7,500	2.62×10^{-12}	37,950
Orange . . .	6,500	3.02×10^{-12}	43,740
Yellow . . .	5,900	3.33×10^{-12}	48,220
Green . . .	5,750	3.42×10^{-12}	49,530
Blue . . .	4,900	4.01×10^{-12}	58,080
Violet . . .	4,550	4.32×10^{-12}	62,580
Ultra-violet . .	3,950	4.97×10^{-12}	71,990

In column 4 the amount of energy absorbed by 1 gm.-molecule of a substance if one quantum were absorbed by each molecule is tabulated. In calculating the above figures, the velocity of light is taken as 3×10^{10} cms. per sec., and N , Avogadro's Number, as 6.06×10^{23} . One gm.-cal. is equal to 4.184×10^7 ergs.

Since the illuminating power of a source is measured in candle-power, the latter being defined as the illuminating power given by a standard source, it is useful to know how many quanta per second correspond to the light of a standard candle. This will, of course, vary with the wavelength of the light used. For this purpose, Gerlach found the amount of energy falling on a surface of area 1 sq. cm. at 1 metre from a standard lamp, and calculated the energy per second associated with one candle-power. This amount of energy, which came out to be 947 ergs per sq. cm. per sec., or 22.6×10^{-6} gm.-cals. per

sq. cm. per sec., is called the "energy candle-power". The number of quanta per second, of light of any wavelength comprised in one energy candle-power can be found, since the energy of one quantum is $h\nu$.

384. Consequences of the Absorption of Light.—When light is absorbed by a system, one or more of several phenomena may occur. The absorption of light means the absorption of energy, and hence the primary effect in all photo-processes is either an increase in the thermal energy of the system or a raising of the electrons in the atoms or molecules composing the system to higher energy levels (a process known as activation, or electronic excitation). The first of these possibilities is not of great importance when the effects of visible light are being considered. Here it is the second effect which is predominant.

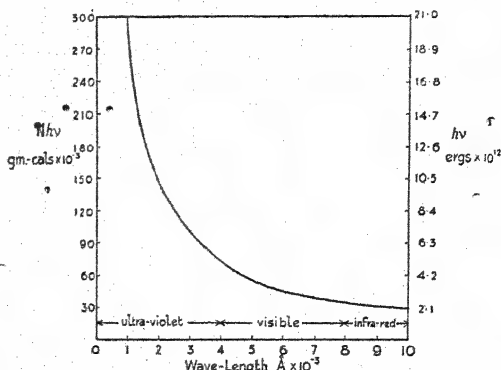
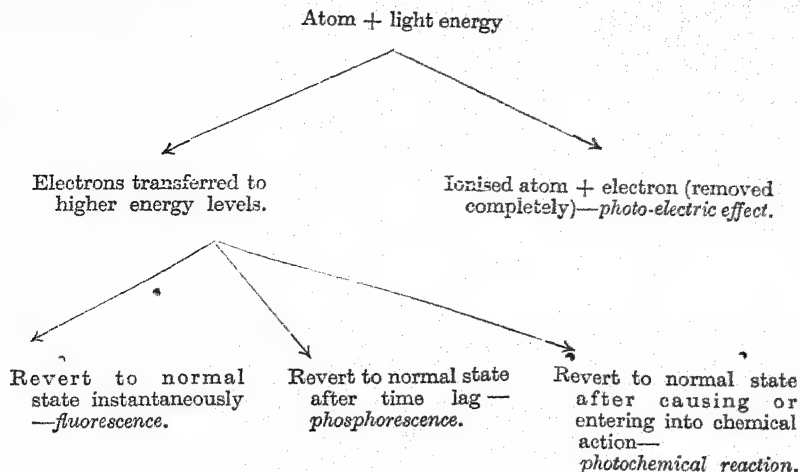


FIG. 223.—Connection between Wavelength and Energy of Quantum.

Photo-processes may be considered under two heads: (a) photo-physical processes; (b) photochemical processes. All photo-processes which do not involve chemical change belong to the first class. When light is absorbed by a body, if it has sufficient energy it will be able to raise certain electrons of the atoms, not only through one or two energy levels, but to eject them completely, thus ionising the atoms. This effect is known as the *photo-electric effect* (§ 386). If the light absorbed is not sufficiently energetic to remove an electron completely it will raise it to a higher energy level, from which it may return to its normal state, either directly or in steps, with emission of energy in the form of light.

This re-emission may be either instantaneous (*fluorescence*) or after a time lag (*phosphorescence*). The energy may, however, be stored by the atom and used for bringing about chemical reactions (*photochemical reactions*), the fluorescence or phosphorescence effects being absent. These facts may be summarised as follows:—



385. Photophysical Change.—We may include under this heading such phenomena as the photo-electric effect, fluorescence, and phosphorescence. Although not strictly chemical phenomena, the chemist must have some knowledge of them, and reference to them here is therefore not out of place.

In dealing with the effects produced by light absorption it is well to realise that whilst the primary effects may be simple, yet these are frequently masked by the occurrence of secondary changes, often of a much more complicated nature. Hence it is that many of the simple laws underlying photochemical and photophysical processes are completely masked, and are therefore difficult to verify. The same behaviour has already been noted in connection with orders of reaction. Whilst we know the simple laws which underlie uni-, bi- and termolecular reactions, we find it difficult to point to many reactions which obey these laws. Thus, only a dozen or so reactions out of the hundreds tested obey strictly the bimolecular law. All the rest are complicated by secondary reactions.

386. Photo-electric Cells.—Light has a peculiar effect on the alkali metals. It was discovered by Hallwachs as far back as 1888 that when light (and particularly ultra-violet light) is allowed to fall on an alkali metal, electrons are given off from the surface of the metal. He did not state his observations in these terms, but that is what actually happens. A type of photo-electric cell is represented in diagrammatic form in Fig. 224. The evacuated glass vessel, *g*, has a mirror of potassium (or some other alkali metal) on one side of its interior. The vessel is also provided with a platinum wire ring. The connections are made through the glass as in the diagram, a sensitive galvanometer and a battery being connected in the circuit. On exposing the cell to light, a current flows

through the circuit owing to the passage of electrons from the alkali metal to the ring, and it is found that (under suitable conditions)¹ the strength of the current is proportional to the intensity of the light.

Of course, photo-electric cells have been greatly improved since their inception, but the principle upon which they work is shown by this simple type. It has been found that the quantum theory provides a very satisfactory explanation of the effect. Millikan, working with a lithium cell, found the e.m.f. it was necessary to apply to oppose the photo-electric current and reduce it to zero. He determined this voltage for light of various wavelengths, and it was found that when the limiting voltage was plotted against the frequency of the light, a straight line graph was obtained (Fig. 225). If it is assumed that one quantum of

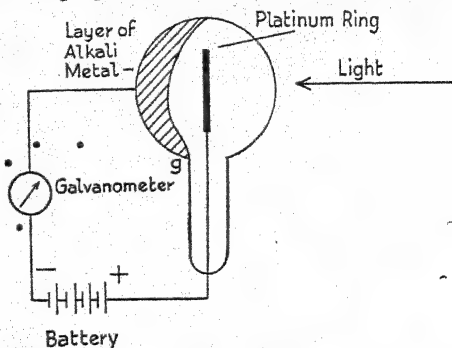


FIG. 224.—Photo-electric Cell (diagrammatic).

light liberates one electron, the energy with which the electron is emitted, V_e , must be equal to the energy of the quantum, $h\nu$.

$$V_e = h\nu$$

where V is the potential under which the electrons are emitted and e is the charge on the electron. In making this equality we have made the assumption that no work is done by the electron in escaping from the surface of the metal ("Austrittsarbeit"). In general, this amount must be taken into consideration. Let us call it β . Then

$$Ve = h\nu - \beta.$$

The values of h and of β can be found from the curve drawn in Fig. 210. Taking, for example, the point A where the opposing potential is zero and ν is 94×10^{13} , and B, where the opposing potential is 0.8 volts and ν is 113.0×10^{13} , we have the following equations:

$$\begin{aligned} 0 &= h \times 94 \times 10^{13} - \beta \\ 0.8 \times 4.77 \times 10^{-10} &= h \times 113.0 \times 10^{13} - \beta. \end{aligned}$$

¹ The current strength is only proportional to the light intensity under special circumstances: (a) The cell must be evacuated (not a so-called gas-filled cell). (b) The applied voltage must be high enough to ensure that the current is saturated, i.e., that all emitted electrons are caught by the ring.

Subtracting the first equation from the second and dividing by 300 to bring the volts into electrostatic units we have

$$h = \frac{0.8 \times 4.77 \times 10^{-10}}{(113.0 - 94.0) \times 10^{13} \times 300} = 6.69 \times 10^{-27}.$$

This agrees very well with the actual value of the Planck constant derived by many other methods (6.548×10^{-27} erg-seconds). β can be derived similarly, and comes out to be 6.2×10^{-12} erg.

What happens in the photo-electric process is that ionisation is produced by the absorption of energy. By the absorption of one quantum the valency electron is completely removed from the atom.

When certain substances are illuminated, it is found that their electrical conductivity is increased. This was first discovered for the element selenium, and the effect was made use of in the selenium cell. But selenium is not the only element that shows the effect, and many

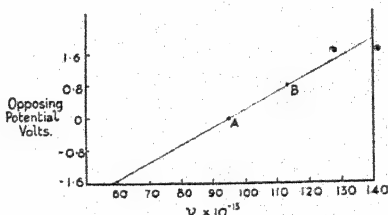


FIG. 225.—Millikan's Curve for Photo-electric Potential against frequency for a Lithium Cell.

crystalline substances [all with a refractive index over 2, and therefore with high electronic deformation (§ 400)] also come into this class. The theory of photo-conduction has not been fully worked out. Probably what happens is that by the action of light electrons are loosened in the space lattice, and on application of a field are capable of migrating through the substance to the electrodes, just as the electrons in a metal (§ 315). The experiments of Gudden and Pohl show that for every quantum absorbed, one electron is set free.

The commercial application of photo-electric cells is most important and interesting, but there is no space to deal with it here in detail. Talking pictures are made possible entirely by the photo-electric effect. The operation of electrical apparatus by light rays at a distance, as in burglar alarms, etc., makes use of photo-electric cells. The discovery of these phenomena ranks next in importance to that of the wireless valve from the point of view of practical application.

387. Fluorescence.—Fluorescence may be regarded as a secondary effect consequent upon the primary process of absorption of a quantum of light by an atom or molecule. In fluorescence, light is absorbed at a certain wavelength and emitted at a greater wavelength. This fact was discovered by Stokes in 1852. There are but few exceptions to this law,

and they can be readily explained (see below). Fluorescein and eosin are stock examples of fluorescent substances, but the phenomenon is shown by a very large number of compounds (including inorganic compounds, such as uranyl sulphate $\text{UO}_2 \cdot \text{SO}_4$) and frequently also in the ultra-violet, so that the fluorescence is invisible. What happens in this process? The molecule absorbs a quantum of energy $h\nu$. This quantity is sufficient to raise an electron to a higher energy level, but not to eject it completely. The electron returns to its original level by steps, going through intermediate orbits. Since these jumps are none of them of such great energy value as the original jump, the wavelength of the emitted light must be greater than that of the absorbed light.

A very interesting case of fluorescence which explains the few exceptions to Stokes' rule was discovered by Franck and Cario in 1923. Mercury vapour absorbs light of wavelength 2536 \AA ., but is not ionised by it. The vapour merely "glows" with that light—the light is emitted at the same wavelength as that at which it was absorbed. This process is called "resonance", and is analogous to acoustical resonance. If mercury vapour is mixed with the vapours of silver, lead, sodium or thallium, and is then irradiated with light of wavelength 2536 \AA ., the vapours of the foreign metals fluoresce. Franck called this "sensitised fluorescence". He showed that when a quantum is absorbed it merely adds itself to the energy already present in the molecule as thermal energy, and enables electrons to be raised to higher energy levels than would be possible with the quantum alone. Thus, we can, in a few cases, induce fluorescence of shorter wavelength than that of the absorbed light, since the energy emitted is not only that of the absorbed quantum, but also that inherent in the system before the absorption.

388. Phosphorescence.—Fluorescence is instantaneous. As soon as the light is absorbed, fluorescence commences, and, as soon as it is cut off, the fluorescence ceases. When we say instantaneous, we mean that the time interval between the two events is not greater than 10^{-8} sec. In the case of phosphorescence a substance, after absorbing light, continues to emit light of another wavelength for some time afterwards. Numerous phosphors can now be made by preparing intimate mixtures of sulphides of the alkaline earth metals with about 2.5 per cent. of alkali chloride, and a trace of the sulphide of a heavy metal. Phosphorescence is best looked upon as slow fluorescence. It is found mainly in solids, as might be expected owing to the greater difficulty of motion. It is found that if fluorescent-substances are fixed by fusion with, say, boric acid and cooling, the masses thus formed phosphoresce.

389. Photochemical Reactions.—It has already been stated (§ 384) that when light is absorbed by an atom or molecule the primary change is the formation of an excited atom or particle:



where A^* represents excited A. This is to be regarded as the primary process in all cases, whether photophysical or photochemical.

As regards primary chemical changes, Einstein assumes, in accordance with the above, that *each molecule entering into reaction has to be excited by the absorption of one quantum of radiation*. This is known as the *law of the photochemical equivalent*. It is necessary to emphasise once again that it applies only to the primary process, and that, in general, secondary processes take place quite independent of the light reaction, and may completely mask the energy change of the primary process. The *quantum efficiency*, γ , of a reaction is the number of molecules actually decomposed per quantum of radiation absorbed. It is sometimes called the *photochemical yield*.

A very great number of photochemical reactions have been studied, and most books on the subject are more or less a collection of the facts with little attempt at systematisation, for it is exceedingly difficult to embrace the many facts in one system. We may, however, classify photochemical reactions roughly into the following classes (after Eggert):—

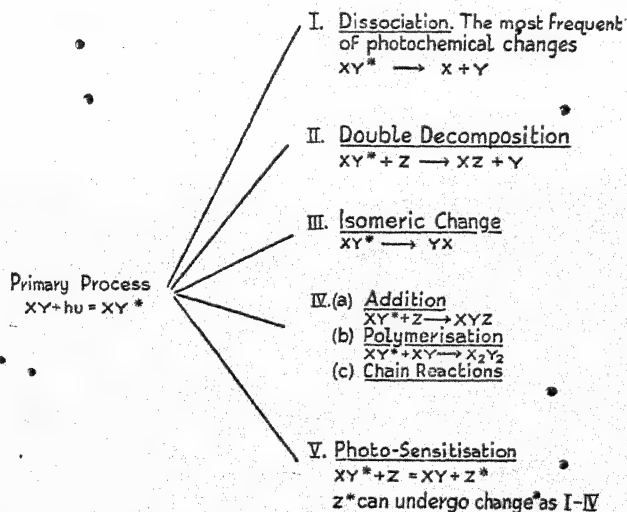
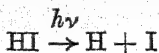


FIG. 226.—Photochemical Processes.

Examples of these various classes will be taken. The velocity of any chemical reaction is the speed at which the slowest stage of it takes place. Now in all probability the excitation of the atom or molecule by the absorption of a quantum is the most rapid part, for it has been shown that the time taken for excitation, if the quanta are available, is less than 10^{-9} second. The speed of the reaction will therefore be dependent largely upon the subsequent chemical reactions.

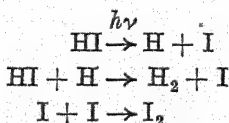
390. Examples of Photochemical Reaction.—The mechanisms of many photochemical reactions are still controversial or not understood. We will, however, consider a number of examples, and starting with decomposition of hydrogen iodide in the gaseous phase. The quantum efficiency of this reaction is 2, and the reaction is brought about by light of any wavelength less than 4,000 Å. It is known from studies of molecular spectra that when a molecule of hydrogen iodide absorbs light of wavelength less than 4,000 Å the molecule dissociates into an atom of hydrogen and an atom of iodine; the latter is in an excited state. The primary process of the reaction is therefore



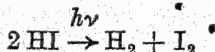
The possible secondary processes that follow this are:



Not all these processes are important. The reactions (3) and (5) are highly exothermic with the result that the products in both cases have such high energies that they will immediately dissociate unless the reaction has taken place in the presence of a third atom. Such three body collisions are, however, unlikely. Reaction (2) is an endothermic process and therefore takes place slowly. The elimination of these three reactions leaves reactions (1) and (4) as the likely secondary processes. The decomposition of hydrogen iodide can now be written as consisting of a primary and two secondary processes.

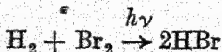


Adding these three equations gives the overall reaction as:

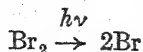


Thus the absorption of one quanta of radiation leads to the decomposition of two hydrogen iodide molecules. This agrees with the measured quantum efficiency.

An example of a photochemical reaction with low quantum efficiency is the formation of hydrogen bromide from hydrogen and bromine.



The quantum efficiency of this reaction is about .02. The primary process is:



the possible secondary processes are:



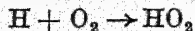
Reaction (2) is endothermic and does not tend to take place. Reactions (3) and (4) depend on the formation of hydrogen atoms in reaction (2) and consequently are very slow. So reaction (1) (although it is a three body type reaction) is the most likely secondary reaction. This is a reversal of the primary process; so most of the bromine atoms formed in the primary process do not lead to the formation of hydrogen bromide (through reactions (2) and (3)); rather do they recombine. The result is that the quantum yield is very small.

The photochemical formation of hydrogen chloride provides a complete contrast to this last example. Hydrogen and chlorine react in the presence of light to give hydrogen chloride. The quantum efficiency is extremely high being between 10^4 and 10^6 . The reaction is explosive in the presence of intense light. The accepted mechanism

for this reaction is that the primary process is $\text{Cl}_2 \xrightarrow{h\nu} 2\text{Cl}$ with the following secondary reactions:



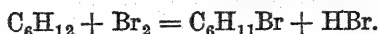
The reactions here are analogous to the secondary processes in the formation of hydrogen bromide. In the present example, however, reactions (2) and (3) take place very easily. The chlorine atom formed in (3) reacts with a further hydrogen molecule to give a repetition of reaction (2), while the hydrogen atom from reaction (2) reacts with a further chlorine molecule to give a repetition of reaction (3). The formation of hydrogen chloride is therefore a chain reaction (§ 215) and this explains the high quantum efficiency. The chain is only broken by reaction (1); this is a three body process which takes place when two chlorine atoms collide on the wall of the reaction vessel. The chains may also be broken by the presence in the reaction vessel of small traces of oxygen. Oxygen leads to chain termination by the reaction



(this radical reacts to form products that do not propagate the chain),

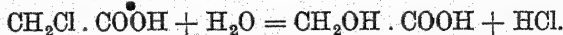
and by the reaction $\text{Cl} + \text{O}_2 + \text{HCl} \rightarrow \text{HO}_2 + \text{Cl}_2$. Examples of other types of photochemical reactions are:

(1) *Double Decomposition*.—The action of bromine on hexahydrobenzene, C_6H_{12} , when illuminated by light of wavelength 4760 \AA ., gives mono-bromhexahydrobenzene and hydrogen bromide.

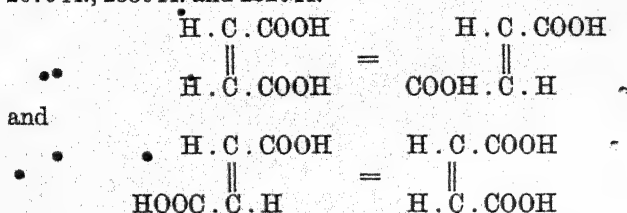


The reaction was investigated by Nernst and Pusch, who found $\gamma = 1.1$, and by Noddack, using light of wavelength 4690 \AA ., who found $\gamma = 1.0$.

The photochemical hydrolysis of monochloroacetic acid is another example of such a reaction,



(2) *Isomeric Transformation*.—This was investigated by Warburg in 1912 with the conversion of maleic into fumaric acid and the reverse reaction, by exposing their aqueous solutions to light of wavelength 2070 \AA ., 2530 \AA . and 2820 \AA .

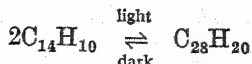


It was found that in the formation of fumaric from maleic acid 0.03 molecule was transformed per quantum, for light of wavelength 2070 \AA ., whilst in the reverse process it was 0.11.

It is clear that as both the forward and the reverse reactions are brought about by the absorption of light, a state of equilibrium will ultimately be reached, when as much fumaric is converted into maleic acid, as the reverse. Such an equilibrium is called a "*photostationary state*". The position of the equilibrium can be calculated from a knowledge of the quantum efficiencies of the forward and the reverse reactions. In this case the equilibrium mixture is found to contain approximately 75 per cent. of maleic acid. The low quantum yields in this photochemical reaction have been explained by Warburg by supposing that the primary action of the light is to separate the molecules into two portions which can then re-unite. Some of them combine to give the isomer, whilst others give the original molecule again. The probability of the latter process is supposed to be considerably greater than that of the former.

(3) *Polymerisation*—a special case of addition. This is illustrated by the polymerisation of anthracene $\text{C}_{14}\text{H}_{10}$, to dianthracene, $\text{C}_{28}\text{H}_{20}$, in solution (benzene, toluene and xylene have been used as solvents). This reaction was investigated by Luther and Weigert (1905), who found

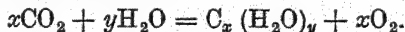
that the polymerisation was reversed in the dark, the dianthracene depolymerising to form anthracene. This reaction goes practically to completion in the dark.



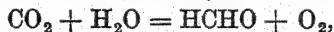
The depolymerisation is a thermal reaction. When a solution of anthracene in benzene is illuminated both reactions will go on until the rates of the reactions become equal and a photostationary state is reached. The value of the quantum efficiency for the reaction given by Weigert is .48 when the wavelength of light used was 3,660 Å.

(4) *Sensitisation*.—As in the case of sensitised fluorescence, the substance which undergoes change in a photochemical process need not necessarily be the absorbing molecule. There may be present something else which does not undergo change, but merely absorbs the energy, and then hands it on to the substances that will react. This process is called *photo-sensitisation*, and is of very great importance.

One of the most important photochemical processes is that which goes on in nature every day, *viz.*, the building up of carbohydrates in plants from carbon dioxide and water in the presence of light. The reaction expressing the change is



It was at first assumed that formaldehyde was the original product



and that this polymerised to carbohydrates. This reaction can be brought about on the laboratory scale, but only very small quantities of carbohydrates are produced. It has been claimed that the production of formaldehyde from carbon dioxide and water under the influence of ultra-violet light has been demonstrated; but even if this can be done in the laboratory, it is quite uncertain whether this can be the mechanism of the reaction in the case of plants, as formaldehyde is a plant poison.

Carbon dioxide and water absorb only in the ultra-violet, as they are colourless. It is thought that their photochemical combination is photo-sensitised by chlorophyll, the green colouring matter of plants. This substance absorbs in the visible, and appears to be able to hand on the energy thus gained to the carbon dioxide and water molecules, causing them to combine even in the absence of ultra-violet light. This is the simplest explanation of the reaction of which the mechanism is not definitely known. Many more complicated explanations have been put forward, in which the chlorophyll plays a definite chemical part.

Another extremely important process based on photo-sensitisation is the use of the cyanine dyes in the manufacture of photographic plates. An ordinary photographic plate is much more sensitive to light of short wavelength than to light of longer wavelength (*e.g.*, the red). It is found, however, that if a small quantity of a special dye-stuff is incor-

porated with the halides in the making of the emulsion, there is a much more even spectral sensitivity. This is due to the fact that the dyestuff absorbs light much more regularly over the visible spectrum than does the halide mixture alone, and it is able to hand on the energy thus gained to the halides and reduce them just as if they themselves had absorbed the light. These plates, which are considerably more sensitive over the whole spectrum range, are called "panchromatic" plates. They are sensitive even to the red light that is used in dark rooms, and so must be worked in complete darkness.

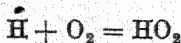
391. The Photochemical Action of X-rays.—Strictly speaking, we should include in the subject of photochemistry the photochemical effects of X-rays. The matter is here, however, considerably complicated by the fact that when X-rays strike any body they give rise to secondary radiations which are themselves photochemically active. The commonest reaction in which X-rays are involved is the photochemical reduction of the silver halides in the photography of X-ray pictures. Many other reactions have also been investigated, and the use of X-rays in medicine (radio-therapy) is based on the biochemical reactions induced by them.

392. Radiation Chemistry.—Radiation chemistry has been defined by Dainton as the study of chemical effects caused by the absorption of the various types of rays emitted in radio-active transformations, or X-rays; that is the study of chemical changes brought about by α , β , γ or X-rays. The subject is similar to photochemistry in that there are two processes; a primary process involving the absorption of radiation and a secondary process involving the reaction of the primary products of radiation.

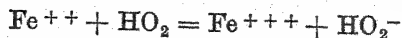
Radiation chemistry differs from photochemistry in that the absorption processes are much more complicated. In photochemistry only radiation of definite wavelengths are absorbed and in solution reactions the radiation is absorbed by the solute only. With radio-active radiations, radiation of all energies may be absorbed by both solvent and solute.

It is believed that the most important products produced in the primary reactions are radicals and atoms rather than ions. Most mechanisms suggested for radiation reactions involve the presence of these uncharged substances.

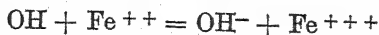
An example of a reaction induced by radiation is the oxidation of ferrous sulphate in aqueous solution by means of γ rays and X-rays. The effect of the radiation on water is to break it down to hydrogen atoms and hydroxyl radicals. If oxygen is absent hydrogen atoms combine to form hydrogen molecules; in the presence of oxygen the reaction



takes place. This is followed by the reaction



Further the OH radicals produced in the primary reaction cause a direct oxidation of the ferrous ion;



Radiations may also lead to the reduction of ferric ion.

The hydroxyl radicals produced by radiation from water can be utilised in hydroxylation reactions. Thus the irradiation with X-rays of a solution of nitrobenzene leads to the production of *o*-, *m*- and *p*-nitrophenols. Hydroxyl derivatives of benzoic acid may be produced similarly. Other reactions induced by radiation are the polymerisations of substances such as vinyl chloride and styrene. For details of such work the reader is referred to articles in the *Annual Reports on the Progress of Chemistry* for 1948 and the succeeding years.

393. The Effect of Ultrasonic Waves on Chemical Reactions.—Richards and Loomis have shown that chemical reaction may be accelerated by sound waves of very high frequency (considerably above the highest audible frequency). This radiation is called supersonic (or ultrasonic) radiation. Sound waves, unlike light waves, are made up of a series of rarefactions and compressions in a material medium. When these waves fall on a molecule the effect will be similar to an increase in temperature. Sound waves are capable of causing the detonation of explosives. This would be expected. There are, however, a number of unexpected reactions, *e.g.*, it is said that the rate of hydrolysis of dimethyl sulphate, $(\text{CH}_3)_2\text{SO}_4$, is accelerated by sound waves of very high frequency.

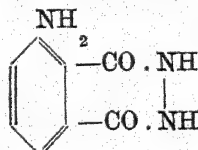
Ultrasonic waves can also cause depolymerisation of highly polymerised substances (such as starch $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, which gives dextrin). The fact that depolymerisation has taken place can be shown by viscosity determinations. The hydrolytic decomposition of sucrose into glucose and fructose is also said to occur in traces when a solution of sucrose is placed in a beam of supersonic waves. Paraformaldehyde, hexamethylenetetramine, gum arabic, and gelatin have also been slightly decomposed by this type of wave-motion.

Ultrasonic waves can alter the conductivity of solutions of electrolytes. Reductions of 20 per cent. in the conductivity of nitrate solutions have been reported. The waves also depolarise electrodes, polarised by a current flow. This depolarisation effect is important in electrolytic processes. The electro-deposition of metals is promoted. The deposits obtained are purer than they are in the absence of the ultrasonic waves. In addition the physical properties, such as tensile strength, of the metals are also affected. These electrode effects occur when the electrodes are situated in a direction perpendicular to the direction of propagation of the sound.

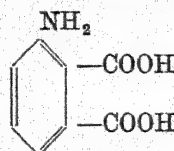
394. Chemiluminescence.—Occasionally when chemical reactions take place, light is emitted. An example of this is the oxidation of phosphorus. This is the reverse process to a photochemical reaction. The light is given out instead of being absorbed. Trautz has collected a list of a number of these changes.

In certain biological reactions light is emitted. The glow of the glow-worm is a case in point.

Of reactions which can be carried out in the laboratory, the most spectacular is the oxidation in alkaline solution of *ortho*-aminophthalic cyclic hydrazide. This substance is a pale yellow crystalline powder, and has the formula



When the hydrazide is dissolved in caustic soda and a little hydrogen peroxide is added, and the liquid dropped from a dropping funnel into an alkaline solution of potassium ferricyanide, as each drop enters the ferricyanide a bright greenish glow is produced. If sodium hypochlorite is substituted for the potassium ferricyanide, the glow is bluish. The chemical changes are complex, but the final product is *ortho*-aminophthalic acid,



Another reaction in which a more feeble glow is emitted is the precipitation of strontium sulphate. A solution of strontium chloride is made, and dilute sulphuric acid is added to it in a dark room.

The most highly luminescent reaction that has yet been observed is the oxidation of the unsaturated silicon compound, silical hydroxide, $\text{Si}_2\text{O}_2\text{H}_2$, by means of permanganate. This was investigated by Kautsky in 1925, who states that the surface luminosity is equivalent to that of a white surface illuminated at a distance of 1.5 metres by a 32 candle-power lamp. In any case, however, the amount of energy liberated in the form of light is very small when regard is had to the amount of substance used.

The light emission from the fire-fly appears to be the most efficient, as judged by eye, because it has a maximum intensity at a wavelength of 5700 Å., at which the eye is most sensitive.

SUGGESTIONS FOR FURTHER READING

- THOMPSON, H. W. "Recent Advances in Infra-Red Spectroscopy." (*Annual Reports on the Progress of Chemistry*, 1945.)
- BOWEN, E. J. "The Chemical Aspects of Light." (*Oxford*, 1946.)
- MACCOLL, A. "Colour and Constitution." (*Quarterly Reviews of the Chemical Society*. Volume I. 1947.)
- COLLINSON, E., and SWALLOW, A. J. "Action of Ionising Radiations on Organic Compounds." (*Quarterly Reviews of the Chemical Society*. Volume IX. 1955.)

CHAPTER XX

THE STRUCTURE OF MOLECULES

395. The Nature of the Problem.—There are two factors about a molecule that are required when we set out to find the structure of the molecule. They are (1) the actual size of the molecule, *i.e.*, the distances apart of its constituent atoms, and (2) the arrangement of these atoms in the molecule. A good deal of information is now available concerning these questions, at any rate, for the simpler molecules.

When we speak of the distance between two atoms in the molecule, we are apt to convey the idea that the atom is a solid ball, as was postulated by Dalton. It is now known, of course, that atoms are assemblages of electrons, protons, and neutrons (§§ 35, 36). How, then, can we speak of the distance between two atoms when the "size" of the atom cannot be defined? It is usual to take the length of a link as the distance between the nuclei of the two linked atoms. We shall then deal not with the true radius of the atom, but with its "effective" radius, the fraction of the length of the link appropriated by each atom.

A. SPECTROSCOPIC METHODS

396. Molecular Spectra.—Information regarding the lengths of linkages may be obtained from a study of spectra.

The general nature of spectra has already been outlined (§ 57). Line spectra are due to energy transitions in atoms, and are comparatively simple. They have been considered already (Chapter III.). An atom cannot emit a band spectrum: this type of spectrum is entirely characteristic of molecules.

A spectrum band consists of a large number of lines which crowd together towards the "head" of the band. There are usually several groups of these bands in a typical band spectrum. The analysis of such a spectrum is a matter of some complexity, and at present it is only possible to calculate structures with any degree of certainty from the spectra of gases or vapours.

The excitation of the molecular spectrum is a rather more complicated matter than would appear at first sight. The very production of the spectrum by passing a discharge through the substance results in the disintegration of the molecule. Consequently, many of the spectra examined have been those of molecules which can have no separate and

continued existence in the laboratory, such as HO, NH and CH, but which have been formed by disintegration of some more complex molecule.

In an atom, the absorption of energy can only result in the transition of an electron from an orbit of low energy to one of higher energy. The reverse of this process gives rise to a line in the emission spectrum. In a molecule, there are two further types of energy change: (1) changes in the energy of rotation of the molecule as a whole, and (2) changes in the energy of vibration of the constituent atomic nuclei relative to one another. All three energy changes are quantised. In general, a line in a band spectrum will be conditioned by all three types, the frequency of the line being determined by the algebraic sum of the three energy changes, but spectra due to molecular transitions of rotational energy alone, or of rotational and vibrational energy without electronic transition are capable of existence, and have been observed.

Considering the rotation spectrum alone, it is to be noted that owing to the quantisation of rotation, the rotation cannot be increased by any arbitrary amount. If the system is rotating, and not emitting, the angular momentum must be a multiple of $h/2\pi$, where h is Planck's constant. For a rigid diatomic molecule it can be shown mathematically that the frequency, ν , of the lines of the spectrum due to purely rotational transitions is given by

$$\nu = \frac{mh}{4\pi^2 I}$$

where m is an integer and I is the moment of inertia of the molecule. For a diatomic molecule,

$$I = \frac{m_1 m_2}{m_1 + m_2} \cdot d^2$$

where m_1 and m_2 are the masses of the atoms and d the distance between them. Clearly, if I can be obtained from observations of the rotation spectrum, d can be found, since m_1 and m_2 are known.

Unfortunately, the pure rotation spectrum lies in the far infra-red, and investigations in this spectral range are difficult. The advent of infra-red photography, however, seems likely to revolutionise this field of investigation. Among the most important of the results obtained are the determinations of the distances between the atoms in the hydrogen halides (Czerny, 1923-27). It is clear that since the moment of inertia, I , involves the masses of the molecules, compounds formed between one element, and various isotopes of another should have slightly different spectral frequencies. Thus there are two chlorine isotopes of mass 35 and 37 respectively; these will form with hydrogen of mass 1, $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$; and with hydrogen of mass 2, $^2\text{H}^{35}\text{Cl}$ and $^2\text{H}^{37}\text{Cl}$. All these hydrogen chlorides should give rotation spectra slightly displaced from

each other, owing to the different masses of the constituent elements. Such isotopic displacements have been observed, not only in the rotation spectra, but also in the rotation-vibration spectra, in which the factor I again appears.

The rotation-vibration spectrum is more easily studied, because it lies mainly in the near infra-red, *i.e.*, the part of the infra-red nearest the visible. If a molecule is regarded as a simple harmonic oscillator, its energy is restricted by quantum considerations to integral multiples of an energy unit, say $h\nu_0$. A pure vibration spectrum is not found, but there are superimposed upon it frequencies due to changes of rotation energy. In deriving the frequency of a line, the algebraic sum of the energies must be used. If the frequency of the lines is represented by ν , then

$h\nu$ = Energy change due to vibrational changes \pm energy change due to rotational changes.

$$= \Delta E_{vib} \pm \frac{mh^2}{4\pi^2 I}$$

$$\text{or } \nu = \frac{\Delta E}{h} \text{ }_{vib} \pm \frac{mh}{4\pi^2 I}$$

where ΔE_{vib} is the change of vibrational energy and m is an integer.

The matter is not, however, quite so simple as this, since, if the vibrational or rotational energy changes, the mean distance between the atomic centres may change, and so must the moment of inertia, I .

Rotation-vibration spectra of polyatomic molecules are very complex. Diatomic molecules with unharmonic binding give bands corresponding to vibrational transitions from $n = 0$ to $n = 1, 2, 3$, etc., n being the vibrational quantum number. Each band has a fine structure due to rotation. From observations of this fine structure, values of I can be deduced for the non-vibrating molecule and also for the vibrating molecule. From I , the nuclear separation can, of course, be obtained; r increases, as would be expected, as the vibrational energy increases (*i.e.*, as n increases).

If a molecule is more complex than diatomic, it will possess more than one moment of inertia, and by observing the fine structure of the rotation-vibration spectrum the values of these moments can be deduced. A linear molecule can be readily differentiated from a triangular one by observing the different moments of inertia. It is also possible to calculate the angles between the bonds.

If electronic changes occur in the molecule, the energy changes due to these must be superimposed upon the vibrational and rotational energy. This makes the spectrum very complex indeed, especially when it is remembered that the moment of inertia of the molecule will be seriously affected by changes in electronic structure.

397. Raman Spectra.—If a beam of monochromatic light is passed through a transparent substance, some of the light is scattered by the molecules in the medium. If this scattered light is examined by means of a spectrometer, it is found that the spectrum is made up of the lines of the original radiation together with a series of lines on either side of them. When the separations of these lines from the line of unchanged frequency are measured, it is found that they correspond to frequencies lying in the infra-red and represent changes in the energy of rotation or vibration. The explanation is that some of the light, on being scattered by the molecules of the medium, picks up or loses one or more quanta of the vibrational or rotational levels. It is thus possible (as it were) to bring the infra-red spectrum into the visible. This phenomenon was predicted by A. Smekal (1923), and was first observed by Sir C. V. Raman (1928).

A great deal of experimental work has been done on the Raman spectra of molecules, which has given valuable information concerning structure. At present, detailed results can only be claimed for the simpler types of molecules. As a result of spectroscopic observations it is known that H_2O , H_2S , ClO_2 and SO_2 are triangular, NH_3 is pyramidal, and COCl_2 , S_2Cl_2 , SOCl_2 and CH_2O are probably Y-shaped.

B. X-RAY AND ELECTRON BEAM METHODS

398. Application of X-ray Methods.—It has already been shown how X-ray interference methods enable the structure of crystals to be deduced. Debye (1929) found that gases and vapours, and also liquids, gave X-ray interference patterns when a technique similar to the powder technique (§ 135) is used. A beam of X-rays, limited by slits, is passed through a vessel through which the gas is flowing, and the interference pattern is obtained on a photographic plate. In the case of a liquid, the results are difficult to interpret, as it is not known whether the scattering is due to atoms in the same molecule or in neighbouring molecules. In a gas, however, the separation between the molecules is much greater than the nuclear separation of the atoms in the individual molecules, and the method can, therefore, be used to find this nuclear separation. It is known that the scattering is not due to the nuclei themselves, but to the orbital electrons, so the distances measured are not the same as those obtained by infra-red spectroscopy. The "centre" of the atom indicated by X-ray interference is the mean centre of the electronic orbits and not the nucleus.

399. Electron-Beam Interference Method.—In dealing with the structure of crystals, it was mentioned that a beam of electrons could be substituted for X-rays in obtaining the interference patterns. This method has been applied to gases and vapours by Wierl (1930), the results agreeing very well with those obtained by the X-ray method,

though probably the latter is the more accurate. The Wierl method has numerous advantages over the X-ray method as regards technique. Since the number of scattering particles is much less in a gas than in a solid, the exposures required in the X-ray method are very long. When first used by Debye, the method required an exposure of twenty-four hours, though this has now been reduced to four to five hours. The electron beam is considerably more intense than the X-ray beam (electrons of 40 kw. energy were used by Wierl), so that the exposure in Wierl's method need only be one-fifth of a second. Also, it would be impossible to use the X-ray method under reduced pressure, as the number of particles would be even smaller than under atmospheric pressure, and the exposure correspondingly longer. The vapours of liquids which boil under atmospheric pressure with decomposition could not therefore be investigated by the X-ray method, whereas results could be obtained by the electron-beam method at reduced pressure.

C. DIPOLE MOMENTS OF MOLECULES

400. The Dielectric Constant.—A study of the dielectric constants of substances has recently given us a great deal of insight into the structure of molecules. It also helps us to understand the process of ionisation, and there is no doubt that it is one of the most important constants characterising matter.

It may be necessary to explain what the dielectric constant is.

If we have two electric charges, e , separated by a distance r in a vacuum, then the force between them will be given by

$$F = e^2/r^2.$$

This force will be one of repulsion if the two charges are of the same sign, and one of attraction if they are opposite in sign.

This law holds only in a vacuum. If we study the force between two charges in any other medium, say air or water, then

$$F = e^2/\epsilon r^2$$

where ϵ is a constant pertaining to the medium, called the *dielectric constant*.

The dielectric constant for air is nearly 1, and so the law of force between point charges is almost the same in air as in a vacuum. In many media, however, the dielectric constant is considerable, and the force is correspondingly reduced. The values of some dielectric constants are given in Table CV. The data for some liquids are also to be found in Table LII.

A system composed of two charged parallel plates is called a "con-

TABLE CV.—DIELECTRIC CONSTANTS

Substance.	ϵ
Plate glass	4.67
Ebonite	3.15
Sulphur	3.84
Mica	6.64
Paraffin wax	2.3
Petroleum	2.0
Water	81.7
Ethyl alcohol	25.4
Air (76 cm. pressure)	1.0006

denser", and has a certain capacity in a vacuum, given by the equation

$$C = Q/V$$

where C is the capacity, Q is the charge and V the potential. If the medium between the plates has a dielectric constant ϵ , then the capacity is given by

$$C = \epsilon Q/V.$$

This provides a useful method of determining the dielectric constant of any medium.

It was discovered by Clerk-Maxwell, in his work on the electromagnetic theory of light, that the dielectric constant of a medium, as determined by the above static method, is intimately connected with its refractive index for radiation of infinite wavelength. The dielectric constant is given in fact by the square of the refractive index, under these conditions, and this has been proved experimentally for many substances.

401. Methods of Determining Dielectric Constants.—This can be but a brief outline. For a more complete account a text-book of physics should be consulted.

The chief methods fall into three classes:—

(1) The measurement of the electric force acting through a dielectric.
 (2) The determination of the velocity of propagation of electromagnetic waves through a material. This is inversely proportional to the square-root of the dielectric constant of the substance. The method merely involves the measurement of the refractive index of the substance (§ 400).

(3) The measurement of the capacity of a condenser when there is

nothing between the plates, and when the latter are separated by a dielectric. The most important methods fall into this class.

In modern times dielectric constants are nearly always determined by finding the capacity of a condenser by an oscillatory circuit method. It is well known that the frequency of oscillation of a circuit depends upon its capacity, its inductance, and its resistance. The frequency of oscillation is fairly easily determined, whence it follows that if the inductance and resistance are kept constant the capacity can be determined by comparison with a standard condenser.

402. Dipole Moments.—Molecules consist of an assemblage of protons, neutrons and electrons. As a rule, the centre of action of the positive parts will not coincide with that of the negative parts of the molecule, and so the molecule may be imagined to consist of a system which reduces to two point charges of equal and opposite sign, separated by a rigid link or rod.

The two charges must of course be equal, otherwise there would be a resultant charge on the molecule. The electrical dipole moment of such a system as that just described is defined as ed , where e is the charge on each end of the rod and d is the length of the rod. This quantity is usually referred to merely as the *dipole moment* of the molecule.

It is clear at once that a knowledge of the dipole moment will tell us a good deal about the constitution of the molecule. Consider a compound formed from two atoms. The atoms themselves before combination are neutral. They have no dipole moment, since every isolated atom must have the centre of action of its positive portion, i.e., the nucleus, at the centre of action of the surrounding electrons. When combination occurs we may suppose that the two atoms become bound by a co-valent link. According to Sidgwick, this means the sharing of two electrons between the orbits of the two atoms. If the bonding electrons are shared equally between the two atoms the resulting molecule will be non-polar, and will possess no dipole moment, for the effective arrangement of the positive and negative portions has not been altered; but suppose that one atom takes a greater share of the two electrons than the other, then the molecule becomes polar, because one atom will have a preponderance of negative electricity associated with it, and the other must, in consequence, have a deficit of negative charge. If then a substance possesses a dipole moment, this indicates that the sharing of the electrons has not been equal.

403. Determination of Dipole Moments.—Let us consider what happens when a gas or vapour is placed in an electric field. First of all, the molecules will, if they possess a dipole moment, tend to set themselves in a direction so that their fields act in opposition to the electric field. The same behaviour is seen exactly with a set of compass needles placed in a magnetic field. They all tend to turn in one direction, so that their north poles point to the south pole of the field. This tendency,

however, on the part of the molecules will be opposed by the thermal agitation of the molecules which makes for random orientation, and also by the effect of the neighbouring molecules on one another. Thus, when the substance is placed in an electric field, it is not to be expected that complete orientation in one direction will be achieved. The extent of it will depend upon the strength of the field, and upon the physical environment of the molecules. This effect is called the *orientation polarisation*. Another effect is to be noted. Whether the molecules possess a dipole moment or not, the electrons will be displaced slightly from their normal orbits and attracted towards the positive pole of the field. This is called the *electron polarisation*. In addition, the nuclei themselves will be slightly displaced relative to each other. This is called the *atomic polarisation*, and is usually small.

We may sum up what we have been saying by noting the existence of the three types of polarisation:—

(1) *Orientation polarisation*, P_o .

(2) *Electron polarisation*, P_e .

(3) *Atomic polarisation*, P_a .

The electron and atomic polarisation together make up the polarisation due to distortion of the molecule, and we may write for their sum, P_d . Hence, the total polarisation

$$P = P_d + P_o = P_a + P_e + P_o.$$

It was shown by Debye that the "Clausius-Mosotti" relationship, which states that the polarisation

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$$

where M is the molecular weight, d the density and ϵ the dielectric constant, measured the total molecular polarisation of the substance. The dielectric constant of the medium will obviously depend on the total effect of the molecules on the field, and this fact finds expression in the above equation. It may be compared with the Lorentz-Lorenz refraction equation (§ 187)

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

where n is the index of refraction and R is the molecular refractive power.

It is clear from what we have said about the effect of thermal agitation on the orientation that the polarisation should vary with temperature; yet no allowance was made for this in the derivation of the above equation. Also, it has been stated that the dipoles will have some influence on each other, and this will clearly depend on their proximity, and therefore on the molecular concentration; yet again there was no allowance for this in deriving the formula.

It is obvious from the above that, in order to measure the permanent dipole moment of the molecule, we must eliminate the electron and

atomic polarisations. If the molecular polarisations of a substance in the vapour and solid state are compared, the approximate value of the orientation polarisation, P_o , can be obtained, since in the solid state there is little or no possibility of orientation, the molecules being firmly held in the crystal lattice. The polarisation in the solid state is due to $P_a + P_s$ alone. P_o can be obtained from the total polarisation P measured for the vapour, by subtracting $P_a + P_s$ obtained for the solid.

When a molecule is exposed to an alternating electromagnetic field instead of to a steady one, if the alternations are very rapid the molecules will not have time to orient themselves, and so the polarisation will be dependent only upon the distortion effect. Ordinary light can be used for the rapidly alternating field, the quantity measured being the refractive index instead of the dielectric constant. The alternations in the visible are too rapid for the heavy nuclei to be displaced and so, if the total distortion polarisation is to be measured, it is necessary to use infra-red light. This then provides a method for distinguishing between P_a and P_s . P_a is found by determining the total polarisation due to distortion using infra-red rays, and then subtracting P_s found for visible rays.

Since the orientation depends on an equilibrium between complete orientation and the effect of thermal agitation, it follows that the orientation will decrease as the temperature is increased and thermal agitation becomes more violent. The exact relation between temperature and the molecular orientation polarisation, P_o , was deduced by Debye in the following form:—

$$P_o = \frac{4\pi}{3} \cdot N \frac{\mu^2}{3kT},$$

where μ is the dipole moment in electrostatic units, N is Avogadro's number, k is Boltzmann's constant (§ 115) and T the absolute temperature. The total polarisation will be

$$P = P_a + \frac{4\pi N \mu^2}{9kT},$$

$$= A + \frac{B}{T},$$

where

$$B = \frac{4\pi N \mu^2}{9k}.$$

If the molecular polarisation is plotted against the reciprocal of the temperature we shall get in all cases a straight line if the above equation is satisfied; but, if the substance is non-polar, then $B = 0$, since $\mu = 0$, and the straight line is horizontal. If the substance is polar, B has a definite value, and the line has a slope from which B can be calculated. It should be noticed that the distortion polarisation is independent of temperature.

Putting the numerical values of N (6.06×10^{23}) and k (1.37×10^{-13}) in the above equation, we have

$$\mu = 0.0127 \sqrt{B} \times 10^{-18} \text{ electrostatic units,}$$

so that μ can be easily obtained from B .

The Clausius-Mosotti relationship states that

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}.$$

Hence, combining this with Debye's equation,

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = A + \frac{B}{T}.$$

For the majority of vapours ϵ is very nearly equal to 1. Thus, for water, at 120°C ., ϵ is 1.004002 e.s.u. Consequently, $(\epsilon + 2)$ is approximately equal to 3. Hence $(\epsilon - 1)$ should vary linearly with $\frac{1}{T}$, since $(\epsilon + 2)$, M ,

and d , as well as A and B , are constant. This, of course, is only approximately true, since $(\epsilon + 2)$ is not quite constant.

The following Table (CVI) contains data for water, methyl and ethyl ethers, and methyl chloride, taken from a paper by R. Sängcr on "New measurements on the effect of temperature on the dielectric constants of gases and vapours" (1929).¹

These figures are plotted in Fig. 227, which shows the graphs between $10^3/T$ and $(\epsilon - 1) \times 10^5$. The linear nature of the curves is in complete agreement with Debye's theory. The curves for carbon tetrachloride and methane are also given in Fig. 227. Both these substances are non-polar, and therefore give a straight line parallel to the temperature axis.

The values obtained for the dipole moments, calculated from the slopes of the curves, are:—

Methyl chloride	$(1.86 \pm 0.03) \times 10^{-18} \text{ e.s.u.}$
Ethyl ether	$(1.10 \pm 0.02) \times 10^{-18} \text{ e.s.u.}$
Water	$(1.84 \pm 0.02) \times 10^{-18} \text{ e.s.u.}$
Methyl ether	$(1.32 \pm 0.02) \times 10^{-18} \text{ e.s.u.}$
Carbon tetrachloride	0
Methane	0

This is the most accurate method of determining dipole moments, but unfortunately the range of temperature required for accurate results is large, and it can therefore only be applied to those substances which do not undergo decomposition within the temperature range used.

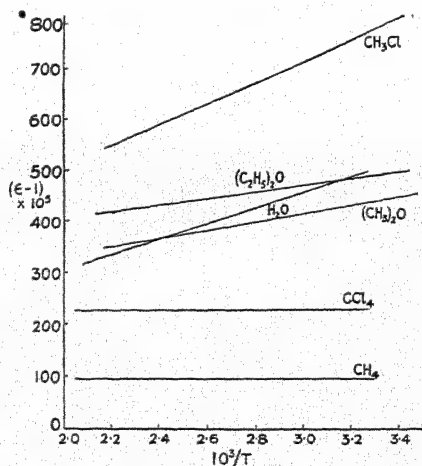
There is another method for measuring dipole moments which does not depend upon the dielectric constant at all, but upon direct measurement of the behaviour of molecules in an electric field. It is called the

¹ This paper is the first in the series of the "Leipzig Vorträge" on "Dipole Moment and Chemical Structure". This series has been translated into English by W. M. Deans (Blackie), under the above title.

TABLE CVI.—VARIATION OF DIELECTRIC CONSTANT WITH TEMPERATURE

Water.			Methyl ether.			Ethyl ether.			Methyl chloride.		
T° Abs.	$10^3/T$	$(\epsilon - 1) \times 10^5$	T° Abs.	$10^3/T$	$(\epsilon - 1) \times 10^5$	T° Abs.	$10^3/T$	$(\epsilon - 1) \times 10^5$	T° Abs.	$10^3/T$	$(\epsilon - 1) \times 10^5$
393.0	2.545	400.2	298.0	3.356	465.5	313.0	3.195	495.0	298.0	3.356	797.6
423.0	2.364	371.7	338.0	2.959	426.7	353.0	2.833	470.0	338.0	2.959	718.3
453.0	2.207	348.8	378.0	2.646	398.1	393.0	2.545	450.7	378.0	2.646	657.8
483.0	2.070	328.7	418.0	2.392	372.2	433.0	2.310	431.0	418.0	2.392	607.2

"molecular beam method",¹ and is based on a method first mentioned by Kallmann and Reiche, and later used by Stern and Gerlach for the determination of the magnetic moment of atoms. By heating in a small oven the substance is obtained in such a state that the molecules are

FIG. 227.— $P - \frac{1}{T}$ Curves for Various Compounds.

far apart from one another, and move along without collision. A beam of such molecules is obtained by allowing them to pass through a very narrow slit into a high vacuum, the beam being further defined by another slit. This beam is passed through an intense non-uniform

¹ For a full account of the use of the molecular beam method, the student is recommended to see Estermann's paper in "Dipole Moment and Chemical Structure", trans. W. M. Deans (Blackie).

electric field when, if the dimensions of the beam and the intensity and inhomogeneity of the field remain fixed, the beam is deviated through an angle dependent upon the electric moments of the molecules. The molecular beam is allowed to impinge on a receiver cooled in liquid air, to which the molecules adhere and leave behind a trace of the solid material, which can be viewed through a microscope. All molecules, irrespective of whether they bear a dipole moment or not, will have one induced in them by the field, but this will only cause a deviation parallel to the direction of the field. The presence of a polar molecule is indicated by a broadening of the trace, and, by a complicated calculation, the two effects can be separated and the dipole moment calculated.

This method has proved useful in the case of substances which are not soluble in non-polar solvents (a condition required for the determination of the dielectric constants of substances at radio frequencies employed in the first method described), or else do not give sufficient vapour to enable the dielectric constants to be measured by the second method. The only condition required is that the substance should be capable of being obtained as a molecular beam. It has been used for the determination of the moments of alkali metal halides, and a notable example is its application to penterythritol.

According to a theory put forward by Weissenberg, a carbon compound of the type CA_4 should be able to exist in two forms, one a regular tetrahedron, with the carbon atom in the centre, and the four A groups at the apices, and the other a pyramid with the carbon atom at the vertex and the A groups at the base. Obviously, a molecule of the first type should possess no dipole moment, whilst one with the pyramidal structure should possess a permanent moment. Penterythritol, $C(CH_2OH)_4$, cannot be examined by the dielectric constant method, being insoluble in non-polar solvents, and decomposing when vaporised under all but very low pressures. Examination of this substance by the molecular beam method, however, shows that its dipole moment is about 2×10^{-18} e.s.u. (Estermann, 1929). Penterythritol acetate also has a moment, but the bromide is non-polar. Estermann states that the observations do not necessarily prove the accuracy of the assumption of a pyramidal model for molecules of the type CA_4 , but do at least show that penterythritol as a whole shows no central symmetry, of which tetrahedral symmetry is one type.

It should be remembered that in all methods of determining the dipole moments of molecules the substance under investigation must either be in the gas or vapour state, or else must be in very dilute solution in a non-polar solvent. This stipulation is necessary in order to eliminate interaction between the molecules themselves. In the usual case in which the substance is investigated in a non-polar solvent, it is necessary to extrapolate to infinite dilution.

404. Results of Dipole Moment Determinations.—It is well to point out exactly what is determined in these experiments. The value obtained is the resultant moment for the whole molecule, and where this is complex, all the links will have contributed to it. The results merely indicate the product ed , where e is the resultant charge at the end of the dipole which has the equivalent length d .

Consider a diatomic molecule, A—B. If an electron were transferred completely from A to B, the dipole moment would be $4.77 \times 10^{-10} \cdot d$, where d is the distance between the nuclei and 4.77×10^{-10} is the charge associated with the electron. The distance between the nuclei will be approximately the molecular diameter, which is about 10^{-8} cms. Hence, the dipole moment of a molecule existing in the ionic state should be in the neighbourhood of 4.77×10^{-18} e.s.u.

The dipole moments of most polar substances are less than this, but in a few cases, higher values have been found. Thus, the dipole

TABLE CVII.—DIPOLE MOMENTS

Throughout this chapter dipole moments are expressed in Debyes. 1 Debye = 1×10^{-18} e.s.u. Thus, when the dipole moment of water is given as 1.85D., this stands for 1.85×10^{-18} e.s.u.

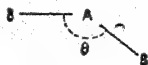
Substance.	Formula.	Moment. (Debye Units)
Methane	CH ₄	0
Ethane	C ₂ H ₆	0
n-Pentane	C ₅ H ₁₂	0
iso-Pentane		
Ethylene	CH ₂ = CH ₂	0
Acetylene	CH \equiv CH	0
Methyl alcohol	CH ₃ OH	1.78
Ethyl alcohol	C ₂ H ₅ OH	1.85
Methyl iodide	CH ₃ I	1.90
Nitromethane	CH ₃ NO ₂	3.8
Acetonitrile	CH ₃ CN	3.51
Acetone	CH ₃ . CO . CH ₃	2.72
Benzene	C ₆ H ₆	0
Chlorobenzene	C ₆ H ₅ Cl	1.53
Nitrobenzene	C ₆ H ₅ NO ₂	3.8
Diphenyl	C ₆ H ₅ — C ₆ H ₅	0
Argon, hydrogen, nitrogen	A, H ₂ , N ₂	0
Hydrogen chloride	HCl	1.03
Hydrogen bromide	HBr	0.78
Hydrogen iodide	HI	0.38
Water	H ₂ O	1.85
Ammonia	NH ₃	1.5
Sulphur dioxide	SO ₂	1.7
Hydrogen sulphide	H ₂ S	0.93
Silver perchlorate	AgClO ₄	4.7

moments of potassium iodide, potassium chloride and sodium iodide, determined by the molecular beam method are 6.8×10^{-18} , 6.3×10^{-18} and 4.9×10^{-18} e.s.u., respectively (Scheffers, 1934). These high values are probably due to deformation of the orbits of the valency electrons. It is clear that the dipole moment gives some idea of the degree of sharing of electrons between the atoms linked. For equal sharing, the moment would be zero.

It has been pointed out by J. J. Thomson that as moments are vector quantities they can be added vectorially, *e.g.*, as in the determination of the resultant of two or more forces by the application of the parallelogram of forces. This method has proved very useful in deciding the moments of various linkages.

Monatomic substances must of course be non-polar; for instance the rare gases possess no moment.

Diatomic molecules (with the exception of elements) are all polar so far as they have been determined. With triatomic molecules we have the possibility of either symmetrical or asymmetrical arrangement, and so the moment may be either zero or finite. Thus, if the molecule is of the type AB_2 , and A lies between two B atoms in a straight line, then the substance will be non-polar if the two links are the same.



I.

II.

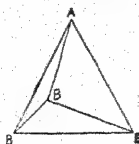
FIG. 228.—Models of Triatomic Molecules.

If, however, one link makes an angle with the other, as in II. above, the molecule will possess a moment given by $M = 2m \cos \frac{1}{2}\theta$, where m is the moment of a single link and θ the angle between them. Water is polar, and must therefore be constructed in this way. Where there are double links, as in $O=C=O$, the linear arrangement of the carbon bonds in the sp hybrid state would mean that this must be a linear molecule, and possess no moment. For this reason CO_2 and CS_2 are not polar.

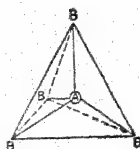
Tetrahedral molecules of the type AB_4 are non-polar if all four atoms lie in one plane, and the angles between the bonds are all equal, as they must be in the case of AB_3 .



Where the model is pyramidal, one atom will lie out of the plane of the rest and the molecule will be polar.

FIG. 229.—Pyramidal Model of AB_3 Molecule.

Hence, the polarity found for ammonia, phosphine, arsine and the trihalides of phosphorus, arsenic and antimony.

FIG. 230.—Model of AB_4 Molecule.

Pentatomic molecules of the form AB_4 should be non-polar on the tetrahedral model or on the plane model. The pyramidal structure would give a finite value of μ . It is found that methane, carbon tetrachloride, silicon tetrachloride, titanium tetrachloride, etc., are all non-polar. Penterthritol, however, has a definite moment (§ 403).

The dipole moment is also a useful criterion in the determination of the contributions of the possible structures in resonating systems. The fact that the nitrous oxide molecule, for example, has a small dipole moment indicates that the molecule cannot consist entirely of either of the two possible structures $\overset{-}{N} = \overset{+}{N} = \overset{+}{O}$ and $N \equiv \overset{+}{N} - \overset{-}{O}$, which would possess high dipole moments, but that there is resonance between the two forms.

The dipole moment has also been used as evidence of hydrogen bonding.

These simple examples of the application of the dipole moment to the elucidation of molecular structure show the value of the method. In the cases we have quoted there is only one type of link, and, of course, the matter becomes much more complicated when we deal with complex organic molecules in which several types of link occur. By making the assumption that the presence of one link does not influence the rest of the molecule,¹ it is possible, by comparing the moments of molecules in which groups are replaced by others, to find the moments associated with individual links. This has been done in very many cases, and a Table of the results taken by permission from Sidgwick's "Covalent Link in Chemistry" is given below:—

¹ It is very probable that deformation of the orbits of the valency electrons often occurs in substances containing an electrovalent linkage, e.g., in potassium iodide. The remarks concerning the dipole moments of linkages, etc., must be understood to refer to covalent compounds.

TABLE CVIII.—DIPOLE MOMENTS OF LINKAGES

H — C 0.2	H — N 1.5 H — P 0.55 H — As 0.15	H — O 1.6 H — S 0.8	H — F (2) H — Cl 1.03 H — Br 0.78 H — I 0.38
	C — N 0.4 C ≡ N 3.3	C — O 0.9 C = O 2.5 C ≡ O 5.3 C — S 1.2 C = S 3.0 C — Se 1.1 C — Te 0.9	C — Cl 1.7 C — Br 1.6 C — I 1.4
P — Cl 0.8 As — Cl 2.0 Sb — Cl 3.9	P — Br 0.6 As — Br 1.7 N = O 1.9		

Knowing the moments of individual links, it is possible to work out the distribution of residual charges in the molecule owing to the unequal sharing of the electrons in the linkages. In the case of hydrogen chloride with the single H—Cl linkage, the moment of this body is 1.03, whilst the distance between the atoms, determined by other means, is 1.27 Å. The moment is the product of one of the residual charges and the distance, and if the residual charge is supposed to reside on the nucleus, then each charge must be $1.03/1.27 = 0.81 \times 10^{-10}$ e.s.u. This can be better expressed as a fraction of the charge on the electron,

TABLE CIX.—RESIDUAL CHARGES

(Taken, by permission, from "The Covalent Link in Chemistry", by Professor N. V. Sidgwick.)

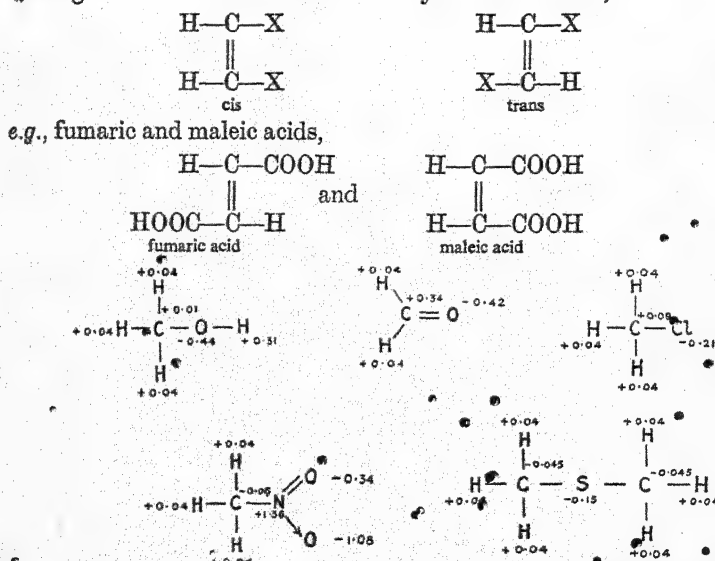
Link.	Moment. $\Delta E \times d$ e.s.u.	Distance. d Å	ΔE e.s.u.	$\frac{\Delta E}{e} = F$.
H—C	0.2	1.14	0.18	0.04
H—N	1.5	1.08	1.4	0.29
H—O	1.6	1.07	1.5	0.31
H—S	0.8	1.43	0.6	0.13
C—N	0.4	1.48	0.3	0.06
C≡N	3.3	1.15	2.9	0.61
C—C	0.9	1.47	0.6	0.13
C=O	2.5	1.27	2.0	0.42
C—S	1.2	1.83	0.7	0.15
C=S	3.0	1.59	1.9	0.40
C—Cl	1.7	1.74	1.0	0.21
C—Br	1.6	1.90	0.8	0.17
C—I	1.4	2.12	0.7	0.15

In the last column, the ratio of the residual charge ΔE on the nucleus to the charge on the electron, e , is calculated.

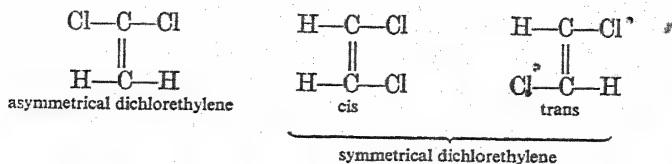
4.77×10^{-10} e.s.u. In this case it is $0.81/4.77 = 0.170$. There will be a charge of $+0.170$ on the H atom and -0.170 on the Cl atom.¹ In this way the residual charges due to various linkages have been calculated, and some of them are given in Table CIX. The positive atom is written first.

These figures enable us to determine roughly the places in the molecule where there is an excess or deficit of charge. In the determination of the residual charges present in molecules which are more complex, the amount for each link must be added. Consider the case of methyl chloride. Each C—H linkage has a charge of $+0.04$ on the hydrogen. This would give for the carbon attached to the three hydrogen atoms a charge of -0.12 . There is another linkage, however, the C—Cl link. This has a charge on the Cl of -0.21 , and a corresponding charge of $+0.21$ on the carbon. Hence the total charge on the carbon is $-0.12 + 0.21 = +0.09$. Where there is a co-ordinate link in the molecule the value 1.0 must be added or subtracted from the appropriate atom. The co-ordinate link adds 1 to the donor and removes 1 from the acceptor. The diagrams below (Fig. 231) have been drawn up in this way (mainly from Sidgwick, "The Covalent Link in Chemistry").

It is obvious that the study of dipole moments can be of great use in deciding questions of *stereoisomerism* in organic chemistry. Thus, in dealing with *cis-trans*-isomerism of ethylene derivatives,



it is clear that the *cis*-form will be polar, whilst the *trans*-form will be non-polar. This has been confirmed by experiment in the case of the dihalogen derivatives of ethylene.



There are three dichloro derivatives of ethylene, the formulæ being shown above. Of these, the first is easily recognised on account of its chemical properties, but the *cis*- and *trans*-forms are not thus recognisable. One of these compounds has been shown to possess a dipole moment of 1.9 e.s.u., and the other zero. The *cis*-form can thus be differentiated from the *trans*-form. This work has been carried out by Errera, who found the following values for the moments of other dihalogen derivatives of ethylene.

Substance.	Moment.
<i>cis</i> -dibromo-ethylene	1.4
<i>trans</i> -dibromo-ethylene	0
<i>cis</i> -diiodo-ethylene	0.8
<i>trans</i> -diiodo-ethylene	0
<i>cis</i> -chlorobromo-ethylene	1.6
<i>trans</i> -chlorobromo-ethylene	0

S.54

Much light is thrown on the question of *benzene substitution* by the study of dipole moments. Benzene itself has no dipole moment, and it is concluded from this and other evidence (supplied by the X-ray structure of hexamethyl-benzene) that the carbon and hydrogen atoms all lie symmetrically in a plane (§ 81).

In the theories of benzene substitution and the positions taken up in the ring by various substituents, put forward by organic chemists, a displacement of electrons in the molecule is assumed. If this does happen, it must be shown in the dipole moments. The moment of a group C—X has been shown in general to be different according as the carbon is part of an alkyl group or an aryl group. Sutton has been able to show that there is a relationship between the difference of the moment of (Ar—X) and (Alk—X), and the directing power of the substituent X. If the moments of which the positive end is remote from the alkyl or aryl group are called positive, and the reverse of this negative, then when the moment of (Ar—X) minus that of (Alk—X) is positive X directs further substitution into the ortho- and para-positions. If the difference is negative it directs further substitution into the meta-position. This behaviour has been explained and is stated

to show that there is an electron drift in benzene when mono-substitution takes place, which decides where future substituents will go.

• TABLE CX.—MOMENTS OF AROMATIC AND ALIPHATIC DERIVATIVES

• (Data taken, by permission, from "The Covalent Link in Chemistry", by Professor N. V. Sidgwick.)

X.	Moment of the linkage (Ar - X).	Moment of the linkage (Alk - X).	Difference $m(\text{Ar} - \text{X}) - m(\text{Alk} - \text{X})$.	Orientation.
CH ₃	+ 0.45	± 0.0	+ 0.45	o & p
NH ₂	+ 1.55	+ 1.23	+ 0.32	o & p
Cl	- 1.56	- 2.15	+ 0.59	o & p
Br	- 1.52	- 2.21	+ 0.69	o & p
I	- 1.27	- 2.13	+ 0.88	o & p
CH ₂ Cl	- 1.82	- 2.03	+ 0.21	o & p
CHCl ₂	- 2.03	- 2.06	+ 0.03	o, p or m
CCl ₃	- 2.07	- 1.57	- 0.50	m
COCH ₃	- 2.97	- 2.79	- 0.18	m
CO	- 3.04	- 2.76	- 0.28	m
C≡N	- 3.89	- 3.46	- 0.43	m
NO ₂	- 3.93	- 3.05	- 0.88	m

It has also been shown that the results obtained in this way give an explanation of the rule put forward by Hammett and Illingworth for the positions of substituents in the benzene nucleus. This rule, to which there are no exceptions, states that: If, in a substitution product of benzene, $\text{C}_6\text{H}_5\text{—X—Y}$, Y is in a later group of the periodic table than X, or if, being in the same group, Y is of a lower atomic weight than X, the direction of subsequent substitution is meta. If Y is in an earlier group, or if there is no Y, then the direction is ortho-para. This is very easily explained on the dipole theory, since the position of an element in the periodic table decides the sign of the dipole formed by it with another element.

The theory has also been applied to the naphthalene and diphenyl derivatives with considerable success.

SUGGESTIONS FOR FURTHER READING

PAULING, L. "The Nature of the Chemical Bond." (Cornell University Press, 1945.)

WELLS, A. F. "Structural Inorganic Chemistry." (Oxford, 1945.)

INGOLD, C. K. "Structure and Mechanism in Organic Chemistry."
Chapters III and IV. (*Bell*, 1953.)

The student is advised to read some of the original papers. These can be discovered by consulting British Abstracts A, or the Chemical Abstracts published by the American Chemical Society. The Annual Reports of the Chemical Society are invaluable.

SUGGESTIONS FOR PRACTICAL WORK AND QUESTIONS

CHAPTER I

SUGGESTIONS FOR PRACTICAL WORK.

Experiment 1.—Determine the equivalents of

- (a) Zinc by replacement of hydrogen in an acid.
- (b) Copper by the displacement method.
- (c) Tin by action of nitric acid and formation of stannic oxide.
- (d) Sodium by the silver chloride method.

Experiment 2.—Determine the density of carbon dioxide.

A round-bottomed flask is provided with a well-fitting rubber stopper, through which passes a piece of glass tubing closed with a piece of rubber tubing bearing a clip (Fig. 231). Weigh the flask full of air, noting temperature and pressure. Now fill the flask with dry carbon dioxide, close it, and weigh again. Now open the clip with the tubing under a strong solution of caustic soda (1 in 3). The solution enters the flask, occupying the volume previously taken up by the gas. There will be a residual bubble of air, which will be under reduced pressure. For accurate results the level of the liquid inside and outside the flask should be the same before closing the clip, but if this is impracticable, the error will be small. Note the volume of the soda solution that entered. For this experiment it is necessary to know the weight of 1 c.c. of air. The results are easily worked out (correct for temperature and pressure). If the weight of 1 c.c. of air is not assumed, the flask must be carefully evacuated and weighed before filling with carbon dioxide.



FIG. 231.—Apparatus for Experiment 2.

Experiment 3.—Determine the density of ammonia.

For this experiment standard solutions of sulphuric acid and of sodium hydroxide are required. The flask, which should be of the type used in Experiment 2, must be filled with ammonia (a gas lighter than air). It is then opened under normal sulphuric acid, which enters the flask, and the clip is closed. The volume of acid entering is noted. The weight of ammonia in it is determined by titrating the excess of acid with normal caustic soda.

Experiment 4.—Determine the vapour density of chloroform by Victor Meyer's method. (See § 12.)

Experiment 5.—Determine the vapour density of benzene by Lumsden's method. (See § 12.)

(a) *Comparative Method.*—Assuming the molecular weight of ether to be 74, it is possible to find that of benzene very easily with Lumsden's apparatus. Weigh empty a small vapour density bottle; then fill it with ether and weigh again. The difference between these two weights gives the

weight of ether taken. Put water into the outer jacket and boil, proceeding as stated above until a constant temperature has been attained. Then introduce the bottle, shut the tap, and determine the increase in pressure. Clean out the apparatus by blowing a current of air through, and then repeat exactly as above for benzene. The calculation of the result has been indicated in § 12.

(b) *Absolute Method*.—The volume of the vaporising tube is first found, and the increase in pressure due to the vaporisation of a known weight of benzene is found just as before. The result is calculated as indicated above (§ 12).

Experiment 6.—Determine the vapour density of acetone by Dumas' method. (See § 12.)

Experiment 7.—Determine the atomic weight of carbon.

The problem resolves itself into two parts: (a) the determination of the equivalent of carbon, and (b) the determination of the valency of carbon by finding the vapour density of its chloride, *i.e.*, carbon tetrachloride.

(a) *Determination of the Equivalent of Carbon*.—It is this part of the work that must be done with as great accuracy as possible.

For this purpose, a known weight of pure carbon is burnt in oxygen and the amount of carbon dioxide formed is weighed. From this it is easy to calculate the equivalent of carbon.

It is first necessary to prepare a pure form of carbon. One of the best for this purpose is sugar charcoal, which is easily made by acting on cane sugar with strong sulphuric acid. The sugar chars, losing water and becoming converted into a form of carbon. The mass is mixed with water and boiled

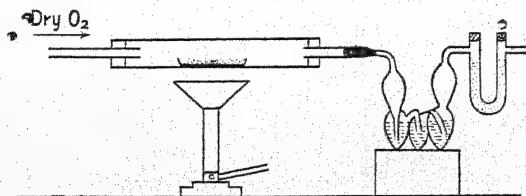


FIG. 232.—Apparatus for determining the Equivalent of Carbon.

in order to dissolve out any unchanged sugar, and is then filtered off. The washing is continued with hot water for some time in order to make quite certain that all unchanged sugar has been removed. The charcoal is then carefully dried in an air oven, heated to 110°C . About $\frac{1}{2}$ gm. of this charcoal is weighed out into a porcelain boat containing some black copper oxide, which is placed in a combustion tube (Fig. 232). The tube is connected at one end with a source of dry oxygen. This may be an aspirator containing oxygen, or, better, a cylinder, the gas being dried by strong sulphuric acid. The other end of the tube is connected to a series of potash bulbs, which are half filled with 30 per cent. potash, and a calcium chloride tube, which are weighed at the beginning of the experiment. The carbon is now heated to redness in the combustion tube, and a slow stream of oxygen is passed over. The stream of gas should be slow enough for the bubbles passing through the bulbs to be counted with ease. When all the carbon has disappeared, the potash bulbs are weighed again. The increase in weight gives the weight of carbon dioxide absorbed. Knowing the weight of carbon from which this originated, it is easy to calculate the equivalent of the element. In order to sweep all the carbon dioxide out of the tube, it is necessary to pass dry air

(carbon dioxide free) through the tube for a few minutes after all the carbon has disappeared.

The second step, that of finding the valency of carbon, has now to be undertaken.

(b) *Determination of the Vapour Density of Carbon Tetrachloride.*—It is essential to use pure carbon tetrachloride. The method used can be either that of Victor Meyer or that of Lumsden. As the boiling point of carbon tetrachloride is about 77°C. , it is necessary to use water, or some heating liquid with a boiling point even higher than that of water, in the outer jacket. The details of this determination are described in § 12.

Having found the vapour density of the chloride, its molecular weight can be found, and, knowing the equivalent, the valency is found as described in § 11, 3a.

Experiment 8.—Determine the atomic weights of silver, potassium, chlorine, bromine, iodine, sodium and lithium, by methods due to Stas.

Although methods are given for the complete determination of the atomic weights of all the above elements, the experiment need not be carried to completion if there is insufficient time. The experiment is easily stopped at any stage.

It is assumed that the atomic weight of oxygen is 16. The method involves the determination of the following ratios:—

KCl : O
KCl : Ag
AgCl : Ag
AgBr : Ag
AgI : Ag
NaCl : Ag
LiCl : Ag.

(a) *Determination of the Formula Weight of KCl.*—Weigh out into a crucible of known weight about 1 gm. of potassium chlorate, and heat, at first gently, then more strongly over a Bunsen until all oxygen is evolved. Allow to cool and weigh. Then reheat for five minutes and weigh again. Repeat this process until a constant weight is reached. The weight of KCl which combines with 48 gms. of oxygen is then calculated, and is the formula weight required. Great care must be taken to avoid loss of chlorate.

(b) *Determination of the Ratio KCl : Ag.*—Weigh out about 2.5 gms. of silver foil, and dissolve it in slight excess of dilute nitric acid. Make the solution up to 500 c.c. This solution will serve for a number of the further determinations. Make a standard solution of KCl of such strength that the potassium chloride and silver nitrate solutions are roughly equivalent. Take 25 c.c. of the silver solution, and titrate it with the standard KCl without the use of an indicator (remember that the AgNO_3 is still somewhat acid). In this way calculate the amount of KCl combining with a given weight of silver, and hence obtain the ratio.

KCl : Ag.

Since we know the formula weight of KCl ($\text{O} = 16$) we have the atomic weight of silver.

(c) *Determination of the Ratio Ag : AgCl.*—Take 100 c.c. of the silver solution and add to it a slight excess of dil. HCl. Boil for a short time, decant off the liquid from the ppt. of silver chloride, and wash the precipitate by decantation. Filter off through a Gooch crucible, the weight of which is known. Take care to keep the precipitate from the light. Wash thoroughly and dry the Gooch and precipitate in an oven, and weigh again. The difference is the weight of silver chloride. Knowing the weight of silver in

the original solution, we obtain the ratio $\text{Ag} : \text{AgCl}$, and knowing the atomic weight of silver we can get the formula weight of silver chloride, and hence the atomic weight of chlorine.

(d) *Determination of the Ratio $\text{Ag} : \text{AgBr}$, and $\text{Ag} : \text{AgI}$.*—In each case take 100 c.c. of the silver solution and add a slight excess of potassium bromide and potassium iodide respectively. Filter off the precipitates of silver bromide and silver iodide, proceeding exactly as above. In this way we obtain the ratios $\text{Ag} : \text{AgBr}$ and $\text{Ag} : \text{AgI}$, and knowing the atomic weight of silver the formula weights of the bromide and iodide can be found, and hence the atomic weights of the elements.

(e) *Determination of the Ratios $\text{NaCl} : \text{Ag}$, and $\text{LiCl} : \text{Ag}$.*—Instructions are given for the ratio $\text{NaCl} : \text{Ag}$. The other determination is exactly the same except that lithium is to be substituted for sodium.

Take about $\frac{1}{2}$ gm. of pure sodium chloride (accurately weighed) and dissolve it in 100 c.c. of water. Then titrate this solution against the silver solution already prepared. As this is slightly acid it is necessary to titrate without an indicator. The result of this titration will give the amount of sodium chloride corresponding to a given weight of silver, and hence the ratio $\text{NaCl} : \text{Ag}$ can readily be found. Knowing the atomic weight of chlorine, the atomic weight of sodium is found by subtraction. In this way the atomic weights of almost any elements can be found. We have given here examples of the determination of seven atomic weights by simple quantitative analysis. It will be noted that they all depend on the atomic weights of silver and chlorine, and hence a slight error in the determination of one of these will cause an error all the way through.

Summary of Results.

$\text{KCl} : \text{O} = 4.659 : 1.000.$	<i>Formula weight of $\text{KCl} = 74.557.$</i>
$\text{KCl} : \text{Ag} = 0.690 : 1.000.$	<i>Atomic weight of $\text{Ag} = 107.88.$</i>
$\text{AgCl} : \text{Ag} = 1.327 : 1.000.$	<i>Atomic weight of $\text{Cl} = 35.457.$</i>
$\text{AgBr} : \text{Ag} = 1.740 : 1.000.$	<i>Atomic weight of $\text{K} = 39.10.$</i>
$\text{AgI} : \text{Ag} = 2.176 : 1.000.$	<i>Atomic weight of $\text{Br} = 79.916.$</i>
$\text{NaCl} : \text{Ag} = 0.542 : 1.000.$	<i>Atomic weight of $\text{I} = 126.92.$</i>
$\text{LiCl} : \text{Ag} = 0.392 : 1.000.$	<i>Atomic weight of $\text{Na} = 22.997.$</i>
	<i>Atomic weight of $\text{Li} = 6.940.$</i>

Experiment 9.—Determine the atomic weight of copper, making use of Dulong and Petit's Law.

The method resolves itself into two parts. First, the determination of the specific heat of copper, and secondly, the determination of the equivalent of the metal.

(a) *Determination of the Specific Heat of Copper.*—It is not necessary to determine the specific heat with any great accuracy, as the Law of Dulong and Petit is at the best only approximately true. For chemical purposes, it is essential to use glass calorimeters, as often the heats of reaction of substances which would attack metal have to be found. For this purpose, two beakers are chosen which fit one inside the other. A layer of felt is placed between the two, and in this way a fairly good glass calorimeter may be made. A much more satisfactory method, however, is to use small thermos flasks as calorimeters. These are quite cheap, and are extremely useful for thermochemical determinations. First of all the water equivalent of the calorimeter has to be determined. This may be done by heating a known weight of water to, say, $50^{\circ}\text{C}.$, and pouring it into a known weight of water in the calorimeter, and noting the highest temperature attained. From these weights and the temperature, the water equivalent of the

calorimeter can be calculated, and when once determined is best noted on a label which is attached to the calorimeter. This saves further determination later on. To determine the specific heat of copper, a piece of copper is weighed, and heated to $100^{\circ}\text{C}.$, by placing it in a test-tube heated for five minutes in boiling water. A piece of thread should be attached to the metal to facilitate its removal from the tube. The temperature of a known weight of water in the calorimeter is taken, and the hot piece of copper is carefully lowered into the water as quickly as possible. The water is stirred, and the highest temperature reached is recorded. There is no need to take into account the cooling correction of the calorimeter, as it is not necessary to get an extremely accurate result. The specific heat of the copper can then be found as shown below.

Calculation of the Water Equivalent of the Calorimeter.—Let the water equivalent be W ; let the mass of water in the calorimeter initially be w_1 gms., and its temperature $t_1^{\circ}\text{C}.$ Let the mass of water added be w_2 gms., and its temperature $t_2^{\circ}\text{C}.$ Let the final temperature be $t_3^{\circ}\text{C}.$

The amount of heat given out by the added water is $w_2(t_2 - t_3)$ calories.

The amount of heat taken up by the calorimeter and contents is $(W + w_1)(t_3 - t_1)$ calories.

Hence $(W + w_1)(t_3 - t_1) = w_2(t_2 - t_3).$

W is the only unknown in this equation, and is readily calculated.

Calculation of the Specific Heat of the Copper.—Let the weight of the copper be w_3 gms., and the weight of water in the calorimeter w_4 gms. Let the initial temperature of the water be $t_4^{\circ}\text{C}.$, and the final temperature $t_5^{\circ}\text{C}.$ The copper is cooled from 100° to $t_6^{\circ}\text{C}.$, and, if its specific heat is s , the amount of heat given out is $w_3s(100 - t_6)$ calories. The water and the calorimeter are heated from $t_4^{\circ}\text{C}.$ to $t_5^{\circ}\text{C}.$, and the amount of heat thus taken up is $(W + w_4)(t_5 - t_4)$ calories. These two amounts are equal. Thus

$$w_3s(100 - t_6) = (W + w_4)(t_5 - t_4),$$

and from this equation s can be calculated.

(b) *Determination of the Equivalent of Copper.*—This is best done by converting a known weight of metal into the oxide, and then calculating weight of metal which will combine with 8 gms. of oxygen.

Weigh out accurately about 0.5 gm. of copper turnings, and dissolve in as small a quantity of 1 : 1 nitric acid as possible. During this operation, which should be carried out in a beaker, care should be taken to prevent loss by spitting. Heat the liquid, which should be diluted to about 100 c.c. with distilled water, to boiling, and then add boiling caustic soda solution until present in excess. Boil the liquid and allow the precipitate to subside. The colour of the liquid above the precipitate should not be green. Decant the liquid through a previously prepared and weighed Gooch crucible, wash the precipitate in the beaker twice with boiling distilled water, and then transfer it to the Gooch. Continue to wash till the washings give no precipitate with silver nitrate. Dry the Gooch in the steam oven, place it inside a nickel crucible, and heat to redness. After about fifteen minutes it is allowed to cool, and is reweighed, the difference in weights giving the weight of copper oxide formed. From this the equivalent of the metal is readily calculated.

QUESTIONS ON CHAPTER I

(1) Describe an experiment which could be carried out in the laboratory to verify the Law of Constant Proportions for one compound.

- (2) How would you determine the equivalent of potassium?
- (3) How has the Law of Conservation of Matter been verified? What are the modern views as to the exactness of this Law?
- (4) In what way does the existence of isotopes affect the Law of Constant proportions?
- (5) What were the assumptions of Dalton's atomic theory? How did the term "molecule" arise?
- (6) What refinements would you introduce into the ordinary laboratory method of determining the volumetric composition of sulphur dioxide to make it one of greater accuracy?
- (7) Give an account of the work of Stas on the determination of equivalents and atomic weights.
- (8) Describe the various methods available for determining the atomic weight of an element which does not form volatile compounds.
- (9) The following facts are known concerning a solid element:—
 - (a) Combined with oxygen it gives a base.
 - (b) Its specific heat is 0.119.
 - (c) 10.00 gms. of the element will unite with 4.298 gms. of oxygen.
 - (d) 8.00 gms. of the element will combine with 10.159 gms. of chlorine.

What conclusions can be drawn from each of these facts concerning the atomic weight of the element?

- (10) In a determination of the atomic weight of iodine, a known weight of silver iodide was converted into silver chloride, which was weighed. In three sets of experiments, the following results were obtained:—

Wt. of AgI.	Wt. of AgCl.
14.41889	8.80228
17.91554	10.93678
10.72744	6.54879

the weights being given in grams. Assuming the atomic weights of silver and of chlorine to be 107.88 and 35.457 respectively, calculate the atomic weight of iodine from these data, correct to three places of decimals.

- (11) In the determination of the atomic weight of lanthanum by Baxter and Behrens, pure lanthanum bromide was added to silver nitrate and the precipitated silver bromide weighed. The following are some typical results:—

Wt. of LaBr ₃ .	Wt. of AgBr.
4.01090	5.96743
5.19186	7.72475
6.57727	9.78548

the weights being given in grams. Assuming the atomic weights of silver and bromine to be 107.88 and 79.916 respectively, calculate the atomic weight of lanthanum.

- (12) Roscoe, in determining the molecular weight of vanadium chloride used Dumas' method, with the following results: weight of globe full of air (9° C., 760 mm.), 24.4722 gms.; weight of sealed globe (9° C., 760 mm.), 25.0102 gms.; temperature of bath when sealing globe, 215° C.; height of barometer when sealing globe, 762 mm.; weight of globe full of water, 194.00 gms. Calculate the molecular weight of vanadium chloride (1 c.c. of air at N.T.P. weighs 0.001293 gms.).

- (13) In the determination of the molecular weight of chloroform vapour

by Hofmann's method, the following results were obtained; weight of liquid in bulb, 0.2704 gms.; volume of vapour, 110 c.c.; temperature of vapour, 99.6° C.; atmospheric pressure, 747 mm.; height of mercury in the tube, 285.2 mm. Calculate the molecular weight of the chloroform.

(14) Hönigschmid and Sachtleben determined the atomic weight of sulphur by synthesising silver sulphide from its elements. Some of the results are given below:—

Wt. of Ag (gms.).	Wt. of Ag_2S (gms.).
7.90291	9.07742
9.74522	11.19355
10.75224	12.35021
9.84439	11.30748

Calculate the value of the ratio $\text{Ag}_2\text{S} : 2\text{Ag}$, and thence the atomic weight of sulphur ($\text{Ag} = 107.880$).

(15) Baxter and Bliss determined the atomic weight of lead from various sources with the following results:—

Sample.	Wt. of PbCl_2 . gms.	Wt. of Ag. for complete precipitation. gms.
Common	2.74332	2.12809
	3.60741	2.79852
Kolm	1.61294	1.25678
	1.60407	1.24983
Uraninite	3.74779	2.91608
	5.63102	4.38436

Calculate the atomic weight of lead from each source, and explain the results.

QUESTIONS ON CHAPTER II

(1) How does a knowledge of the Laws of Electrolysis lead to the conception of the discrete nature of electricity? How has the charge on the electron been determined?

(2) What radiations are given off from radium? How is the nature of each radiation confirmed, and how does the radiation fix the nature of the element formed by the disintegration?

(3) How is it known that the electron is an elementary constituent of all matter?

(4) Describe the historical development of the nuclear theory of the atom.

(5) What is an isotope? What experiments have been made in an endeavour to separate isotopes?

(6) Write an essay on atomic transmutation.

(7) What do you understand by the "physical" atomic weight of an element? How may it be determined?

(8) What was Prout's Hypothesis? Discuss it from the point of view of our modern conception of the structure of the atom.

(9) What is meant by a radioactive series? Explain what happens with regard to the structure of the atom when disintegration takes place.

(10) Give an account of the phenomenon of nuclear fission.

(11) Describe the use of radioactive isotopes as tracers in chemical experiments.

QUESTIONS ON CHAPTER III

- (1) Describe the evidence afforded by a study of spectra concerning the nature of the atom.
- (2) Show how the various line series in the hydrogen spectrum have been explained.
- (3) How are the electrons in an atom of an element arranged about the nucleus? What is the relationship between the electronic configuration of such an atom and the position of the element in the periodic table?
- (4) Discuss the application of wave mechanics to the structure of the hydrogen atom.

QUESTIONS ON CHAPTER IV

- (1) Discuss the statement that "the valency is the quotient of the atomic weight by the equivalent".
- (2) Trace the development of the theory of valency.
- (3) What do you understand by electrovalency, covalency, semi-polar linkages? Give examples of compounds in which these linkages occur.
- (4) What are the main differences between electrovalent and covalent compounds? Explain them as far as possible.
- (5) Give an account of the action of water on the halides.
- (6) What is meant by "chelate compounds"? Give examples.
- (7) Why is it that the radical (XO_4) is of such frequent occurrence in inorganic compounds? Show why it possesses special stability.
- (8) Explain the occurrence of association in water? By what means would you show that water was associated? (See Chapter IX.)
- (9) What are the characteristics of an ionising solvent? Discuss the solubility of substances in water and in other solvents, classifying substances according to their nature and the type of solvent which dissolves them. (See Chapter XIV.)
- (10) Give an account of the molecular orbital theory of valency.
- (11) Describe what is meant by the term "resonance"; how is this concept important in accounting for the structure of conjugated molecules?

CHAPTER V

SUGGESTIONS FOR PRACTICAL WORK

Experiment 10.—Determine the heat of neutralisation of (a) sodium hydroxide by hydrochloric acid, and (b) sodium hydroxide by acetic acid.

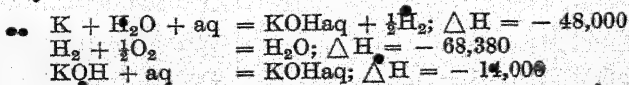
Experiment 11.—Determine the heat of solution of ammonium chloride.

Experiment 12.—Determine the heat of precipitation of silver chloride.

Experiment 13.—Determine the basicity of phosphoric acid. The method that can be applied for the performance of these experiments is described in § 97. It will require but little modification to suit each experiment.

QUESTIONS ON CHAPTER V

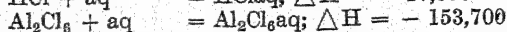
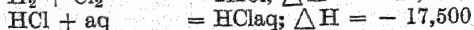
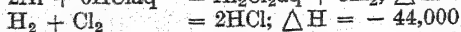
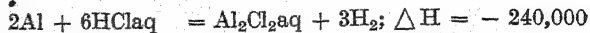
- (1) What is meant by heat of formation and heat of combustion? Calculate the heat of formation of potassium hydroxide from the following data:—



(2) What differences are to be noted between chemical compounds according as they are formed with evolution or absorption of heat? Describe the commercial preparation of an endothermic gas.

(3) How can it be shown whether heat is absorbed or evolved in the dissociation of phosphorus pentachloride?

(4) Calculate the heat of formation of anhydrous aluminium chloride from the following data:—



(5) The heat of precipitation of AgCl is the same no matter whether it is prepared by any of the following methods:—

(a) addition of silver nitrate to hydrochloric acid;

(b) addition of potassium chloride to dilute silver nitrate;

(c) addition of silver sulphate to sodium chloride solution;

(d) addition of barium chloride solution to silver chlorate solution.

Explain this.

(6) Describe how you would determine the heat of neutralisation of an acid by a base. Of what importance is this determination?

(7) In what way is the heat of reaction connected with the variation of the equilibrium constant of the reaction with temperature. Give examples of the use of this relationship to determine heats of combustion or formation.

(8) What is Hess's Law? The heat of solution of anhydrous strontium chloride is $-11,000$ gm.-cals., and that of the hexahydrate $7,300$ gm.-cals. Calculate the heat of hydration of the anhydrous salt to hexahydrate.

(9) Calculate the heats of formation of ethane, ethylene, and acetylene respectively from their elements at 17°C . (a) at constant pressure, (b) at constant volume, given the following heats of combustion: ethane $-370,350$ gm.-cals.; ethylene $-333,350$ gm.-cals.; acetylene $-310,000$ gm.-cals.

Heats of formation: carbon dioxide, $-94,380$ gm.-cals.; liquid water, $-68,380$ gm.-cals.; all taken at constant pressure.

QUESTIONS ON CHAPTER VI

(1) What do you understand by a reversible process in the thermodynamic sense?

(2) What do you understand by chemical affinity? How would you measure the affinity of a reaction? (See Chapter XVI.)

(3) What is the significance of entropy and how is the entropy of a system measured?

QUESTIONS ON CHAPTER VII

(1) What are the assumptions of the kinetic theory of gases, and how far are they justified? Show how Boyle's Law may be derived on the basis of this theory.

(2) What alterations in the other gas laws are necessitated in consequence of the fact that Boyle's Law does not hold with accuracy?

(3) What information concerning the atomicity of a gas can be obtained from a knowledge of its specific heats? Describe one method by which the ratio of the specific heats for a gas can be obtained.

(4) What do you understand by the terms "mean free path", "root-mean-square velocity"?

(5) Show how Graham's Law of Diffusion may be derived from kinetic considerations. Would you regard it as a true law, or are there deviations from it?

(6) Moles and Salazar (1932), found the density of carbon monoxide under a pressure of one atmosphere and at 0°C. , to be 1.25010 gms. per litre. The value for $(1 + \lambda)$ was 1.0050. The gram-molecule occupies a volume of 22.414 litres. Calculate the molecular weight of carbon monoxide and the atomic weight of carbon.

(7) Caywood and Patterson (1933), give the following results for normal densities and "effective" compressibility coefficients:—

Gas.	Normal Density. (gm. per l.)	$1 + \lambda$.
Ethylene	1.2606	1.0073
Carbon dioxide	1.9767	1.0066
Nitrous oxide	1.9777	1.0071
Sulphur dioxide	2.9265	1.0249
Dimethyl ether	2.1100	1.0281

Calculate the molecular weights of these compounds, and the atomic weights of carbon, nitrogen and sulphur.

QUESTIONS ON CHAPTER VIII

(1) How would you attempt to determine the molecular weight of a solid? How far can a solid be said to possess a molecular weight?

(2) How has the structure of crystals been investigated? Outline some of the important results that have arisen from this work.

(3) Define the term "allotropy". What classes of allotropy can be distinguished?

(4) Discuss the allotropy of nitrogen, sulphur, phosphorus, and hydrogen.

(5) What energy considerations govern the existence of stable and metastable states, and how are these reflected in the physical properties of substances in the various states?

(6) What is meant by the term "isomorphism"? To what use can a study of this phenomenon be put?

(7) Write an essay on the specific heats of solid elements.

CHAPTER IX

SUGGESTIONS FOR PRACTICAL WORK

Experiment 14.—Determination of the critical temperature of carbon dioxide.

Procure a thick walled capillary tube containing some liquid carbon dioxide. Place it in a water bath, and gradually raise the temperature of the water until the boundary between liquid and gas just disappears. Take the temperature of the water.

Experiment 15.—Effect of pressure on the boiling point of a liquid.

Fit up an apparatus for distillation of water *in vacuo*, complete with manometer. Reduce the pressure, and take the boiling point of the water in the usual way, reading the manometer at the same time. Allow a little air to enter, and again determine the boiling point. Do this at intervals up to atmospheric pressure.

Experiment 16.—Determine the molecular volume of ethyl acetate.

The instructions for this are given in § 173. The most difficult part of this experiment is filling the bulb-tube.

Experiment 17.—Compare the surface tensions of water and benzene.

Use the drop weight method described in § 175. Make sure the apparatus is quite clean before attempting a determination. If the surface tension of water is known (72 dynes per cm. may be taken as a rough figure), the absolute surface tension of benzene may be calculated.

Experiment 18.—Determine the viscosity of benzene.

Use the viscometer described in § 181. Find the viscosity of water from the tables, and calculate the absolute viscosity of benzene.

QUESTIONS ON CHAPTER IX

(1) Show how the critical temperature and pressure can be calculated from van der Waals' equation.

(2) How may the critical pressure, temperature and volume of a gas be determined?

(3) Write an essay on the liquefaction of gases, pointing out the chief methods available, and the principles upon which they are based.

(4) What properties of liquids may be made use of in determining chemical constitution? Describe the experimental work necessary in the investigation of any one of these properties.

(5) In what ways does a knowledge of surface tension assist in deciding chemical constitution?

(6) By what methods may the molecular condition of a liquid be investigated?

(7) What do you understand by the term "association"? What types of liquids are associated? Indicate how the degree of association may be determined.

(8) Calculate the molecular viscosity of propionic acid $C_2H_5.COOH$ from the data given in § 182. The observed value was 630.

(9) Calculate the parachors of the given substances from the data in § 178. The observed values are given in brackets. (a) Ethylene ($CH_2 = CH_2$) (99.5); (b) acetone ($CH_3.CO.CH_3$) (161.5); (c) nitrosyl chloride, $(Cl - N = O)$ (108.1).

(10) The following data are known for the fluorides of sulphur, selenium and tellurium:—

	Density of Liq., <i>D</i> , gm./c.c.	Density of Vapour, <i>d</i> , gm./c.c.	Surface Tension γ , dynes/cm.
SF_6	1.975	0.009	13.78
SeF_6	2.340	0.011	13.71
TeF_6	2.67	0.013	13.23

Find the parachors of the fluorides.

(11) The viscosity of nitromethane is 0.00627 poise at 25° C. Its density is 1.1312. The formula is CH_3NO_2 . What conclusions do you draw as to its molecular complexity in the liquid state?

(12) The viscosity of nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) is 2.0380 centipoises at 19.50° C. Its density is 1.2. Is this liquid simple, or associated?

CHAPTER X

SUGGESTIONS FOR PRACTICAL WORK

Experiment 19.—To study the equilibrium between ethyl alcohol, acetic acid, ethyl acetate and water.

Set up a thermostat for 60° C. Draw off three test-tubes, and place in them (1) about 3 gms. of absolute alcohol, and 1 gm. of glacial acetic acid; (2) 2 gms. of glacial acetic acid, and 2 gms. of absolute alcohol; (3) 3 gms. glacial acetic acid, and 1 gm. of absolute alcohol. Seal off the tubes and place them in the thermostat for a day. Remove them from the thermostat and break them open under water. Titrate each solution with normal caustic soda. Also titrate a known weight of glacial acetic acid with the same solution. Calculate the concentrations of acid, alcohol, ester and water at equilibrium, and see if they obey the Mass Law. (Theory, §§ 208 and 202.)

Experiment 20.—To study the rate of transformation of N-chloroacetanilide into p-chloroacetanilide.

First prepare some N-chloroacetanilide by the following method. Suspend a weighed quantity of acetanilide in excess of a solution of potassium bicarbonate and add the calculated quantity of bleaching-powder solution which has been standardised against thiosulphate. Extract the product with chloroform, and recrystallise from a mixture of chloroform and petroleum ether; m.p. 91° C. Set a thermostat for 25° C. Dissolve 16–20 gms. of the N-chloroacetanilide in 100 c.c. of 20 per cent. acetic acid in a small flask, which is then corked and placed in the thermostat. One hundred c.c. of a normal solution of hydrochloric acid in a similar flask are also placed in the thermostat. When the two flasks have attained the temperature of the thermostat (an interval of half an hour should be allowed), the two solutions are mixed and the time taken. Immediately withdraw 5 c.c. of the solution and run it into an excess of acidified potassium iodide, and titrate the liberated iodine with standard thiosulphate. Further portions of 5 c.c. are withdrawn at intervals of 10, 20, 30, 45, 60, 90 and 120 minutes, and the above procedure repeated. Calculate the amount of substance left after each time. This will be $(a - x)$. Calculate the amount at time 0, this will be a . Actually, there is no need to calculate the absolute concentrations, since the titrations are proportional to these. See whether the results best fit the bimolecular, or the unimolecular, equation. (Theory, §§ 207 and 212.)

Experiment 21.—To study the rate of inversion of cane-sugar.

Dissolve 20 gms. of cane-sugar in water, and make up to 100 c.c. Prepare also a normal solution of hydrochloric acid. Put two flasks, containing 50 c.c. of each solution respectively, in a thermostat set for 25° C., and when they have attained this temperature, mix the solutions and pour into a polarimeter tube, which can be surrounded by a water jacket, through which flows water at 25° C. Take the rotation as soon as possible, and then

at intervals of five minutes for half an hour, then at intervals of fifteen minutes. Take a final reading after the tube has been allowed to stand for two or three days. This gives r_{∞} . Calculate the values of $r - r_{\infty}$, and work out the constant from the equation

$$k = \frac{1}{t} \log_e \frac{r - r_{\infty}}{r_x - r_{\infty}} = \frac{2.303}{t} \log_{10} \frac{r_a - r_{\infty}}{r_x - r_{\infty}}$$

(Theory, § 207.) Pure sugar should be employed.

Experiment 22.—Investigate the rate of decomposition of hydrogen peroxide.

Hydrogen peroxide does not decompose at an appreciable rate at ordinary temperatures without the addition of a catalyst. A suitable catalyst is colloidal platinum, which is easily prepared by sparking between two platinum wires under water (or see § 350).

Take about 50 c.c. of "20 volume" hydrogen peroxide and make up to 1 litre. Take 100 c.c. of this in a conical flask and place in the thermostat at 25° C. Add 2 c.c. of colloidal platinum, and withdraw 5 c.c., mix it with excess of dilute sulphuric acid and titrate with N/20 permanganate. Note the time at which the withdrawal was made, and take further quantities of 5 c.c. at intervals of five minutes, or at increasing intervals. Calculate the amount of hydrogen peroxide left at each time, and see whether the data obtained fit the unimolecular equation. Instead of calculating the concentration the actual titre may be used. To obtain the initial concentration, titrate some of the original solution with the permanganate before adding the catalyst.

The effect of temperature on this decomposition may also be studied by repeating the experiments with a further quantity of hydrogen peroxide placed in a thermostat regulated for a different temperature. If the temperature is now made 35° C., the temperature coefficient may be obtained. (Theory, § 207.)

Experiment 23.—To study the rate of hydrolysis of ethyl acetate by an alkali.

Prepare some N/2 sodium hydroxide solution free from carbonate. The solution must be kept free from air, and may be used in an automatic burette (see A. J. Mee, *School Science Review*, December, 1933). After standardising this, measure out enough to prepare 250 c.c. of N/10 sodium hydroxide in a measuring flask, and made up to the mark. Dissolve 4.4 gms. of freshly distilled ethyl acetate in 500 c.c. boiled distilled water. This will make an N/10 solution. Put 200 c.c. of each solution in separate conical flasks capable of holding 500 c.c., and put both in the thermostat at 25° C. Whilst these are attaining the temperature of the bath, measure out 25 c.c. of N/10 hydrochloric acid into five small conical flasks. Now mix the ethyl acetate and the sodium hydroxide thoroughly, take the time, withdraw 25 c.c. and run it into the acid in one of the small flasks. This immediately stops the reaction. The time should be taken when the pipette is half empty. Now titrate the excess of acid by means of N/10 sodium hydroxide free from carbonate. Take out other portions at intervals of a quarter of an hour.

Calculate the velocity constant from the bimolecular equation. (Theory, § 208.)

Experiment 24.—Examine the reaction between sodium formate and silver acetate.

Prepare N/10 solutions of sodium formate and of silver acetate, and standardise them by the usual methods. Set a thermostat for 80° C. Take

100 c.c. of each solution in separate conical flasks, and allow them to attain the temperature of the thermostat. The flasks should be securely corked. Mix, and note the time. Withdraw 10 c.c., run it into cold potassium thiocyanate (50 c.c. of N/10), and note the time when the pipette is half empty. Titrate the excess thiocyanate with standard silver nitrate. Calculate the concentrations of formate and acetate left, and see if the reaction follows the termolecular equation,

$$k = \frac{1}{2t} \cdot \left\{ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right\}.$$

(Theory, § 209.)

Experiment 25.—Determine the order of the reaction $6\text{HI} + \text{HBrO}_3 = 3\text{H}_2\text{O} + 3\text{I}_2$.

This is done by determining the time taken to complete a given fraction of the reaction. Prepare N/10 solutions of potassium iodide, potassium bromate, and hydrochloric acid, and a N/100 solution of thiosulphate.

In a 350-c.c. conical flask place 25 c.c. of the iodide solution and 100 c.c. of acid, and add 100 c.c. of water. In another similar flask place 25 c.c. of bromate solution, and put both flasks in the thermostat at 25° C. When both have attained the temperature of the bath, mix, and note the time of mixing. At intervals of two, and later five, minutes, take out 25 c.c. of the mixture, run it into 50 c.c. of ice-cold water to stop the reaction. Determine the amount of iodine by titration with thiosulphate.

Now prepare another solution with only half the concentration of bromate, i.e., 50 c.c. iodide, 200 c.c. of hydrochloric acid, and 225 c.c. of water and 25 c.c. bromate. Repeat the observations with this mixture.

From the results of the titrations, calculate the number of gram equivalents of hydrogen iodide used up. Plot these against the time in minutes, and find the time taken for, say, one-third of the hydrogen iodide to be oxidised in both cases.

The product of the concentration of the reactants in the first case is twice that in the second, and so, if the reaction is bimolecular, the time required for any definite fraction of the reaction to be completed should be twice as great in the second case as in the first. See whether this is the case. (Theory, § 207.)

SUGGESTIONS FOR FURTHER PRACTICAL WORK

Investigate the following:—

- (a) The reduction of ferric chloride by stannous chloride.
- (b) The order of the reaction in the case of hydrolysis of methyl acetate by means of an acid catalyst.
- (c) The temperature coefficient of the hydrolysis of ethyl acetate by sodium hydroxide.
- (d) The mutarotation of glucose.
- (e) The catalytic decomposition of hydrogen peroxide using the gas burette to determine the volume of oxygen evolved in a given time.
- (f) The order of the reaction given under (a) by taking excess of the reagents in turn.

QUESTIONS ON CHAPTER X

- (1) What do you understand by a reversible reaction? Give examples of such reactions.

(2) What contributions were made to chemistry by Berthollet, Berthelot, and Guldberg and Waage? State the Law of Mass Action, and show how it may be derived qualitatively from the kinetic theory.

(3) What are the factors which influence chemical equilibrium? Illustrate your answer by examples.

(4) Illustrate the importance of the Law of Mass Action in technical processes.

(5) What do you understand by the order of a reaction? Show how you would determine the order of the reaction between methyl alcohol and acetic acid.

(6) What is a unimolecular reaction? Give examples of this type of reaction. What explanation of them has been given?

(7) Give an account of the radiation theory of chemical reaction, and explain its defects.

(8) What is meant by heat of activation? How can it be determined?

(9) What is the importance of a knowledge of the temperature coefficient of a chemical reaction?

(10) The following data have been obtained for the thermal decomposition of malonic acid, which takes place according to the equation

$$\text{CH}_2(\text{COOH})_2 \longrightarrow \text{CH}_2\text{COOH} + \text{CO}_2$$

<i>t</i> , min.	10	20	35	56	∞
Pressure, mm.	37.0	67.0	108.0	155.0	302.0

Find the order of the reaction. All the reactants are in the vapour phase. (The data are due to Hinshelwood.)

(11) The following data have been obtained for the reaction between acetic anhydride and water (Sidgwick and Rivett):

<i>a</i> = 0.1160				
<i>t</i> = 0	87	417	544	852 secs.
<i>x</i> =	0.02378	0.07748	0.08848	0.10360

a is the quantity of acetic anhydride present initially, and *x* that used up at time *t* after the commencement of the reaction, both quantities in gram-molecules. Find the order of the reaction, and whether it agrees with the chemical equation. If not, attempt an explanation.

(12) How would you attempt to find the order of the reaction between chloroform and alcoholic potash? What result would you expect to find, and why?

(13) The following results for the velocity constant of the reaction



were found by Daniels and Johnston.

Temp. ° C.	65°	45°	25°	0°
<i>k</i>	0.292	0.0299	0.00203	0.0000472

In calculating *k*, the times were expressed in minutes. Calculate the heat of activation from these results.

(14) Hinshelwood and Burk found the following values for the effect of temperature on the velocity constant of the reaction

$$2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$$

Temp. ° Abs.	1,125°	1,053°	1,030°	1,001°	838°
Log ₁₀ (<i>k</i> × 10 ³)	4.064	3.223	2.940	2.580	0.040

The times were measured in seconds, and the concentrations in gram-molecules per litre. Calculate the heat of activation for the two gram-molecules, assuming that the Arrhenius equation holds at these temperatures.

(15) In determining the rate of reaction of ethyl bromide and potassium hydroxide, equal quantities of N/10 solutions of the reactants were used, and 20 c.c. of the reacting liquid were withdrawn at definite times (t) from the start, and titrated with $\frac{N}{10}$ acid. The volume of acid, x , required is shown in the table:—

Time t , mins.	x .
0	20.0
21	14.71
46	11.14
97	7.42
164	2.92

Calculate the order of the reaction and the value of the velocity constant. (The data are due to Hinshelwood and Grant.)

(16) Blandon and Thompson investigated the order of the reaction between methyl iodide and pyridine. The following data were obtained:—

a and b are the concentrations in gram-molecules per litre of methyl iodide and pyridine respectively.

t is the time, in minutes,

x is the concentration, in gram-molecules per litre, of the quaternary iodide ($C_5H_5NCH_3I$) formed.

The reaction was carried out at 60° C.

$$a = 0.03222$$

$$b = 0.3013$$

t	57.5	89.5	135.5	182.5	228.5
$\cdot 10x$	0.282	0.401	0.536	0.648	0.721

Make calculations to see whether this reaction follows the bimolecular law, and calculate the velocity constant.

CHAPTER XI

SUGGESTIONS FOR PRACTICAL WORK

Experiment 26.—To determine the transition point between rhombic and monoclinic sulphur.

Although the experimental methods of determining transition point are given in Chapter VIII., the actual work is best carried out here, as it is a Phase Rule problem.

The simplest method is the dilatometric method, and the simple dilatometer described by Sherwood Taylor ("Elementary Practical Physical

Chemistry", p. 76) may be conveniently employed. It is made by connecting a test-tube with a fairly long capillary tube which has been bent at right angles as shown in the diagram.

Boil some sulphuric acid (1 to 3) to free it from air. Powder some roll sulphur, and put it in the tube (about two-thirds of the tube should be full). Add some of the sulphuric acid, and warm to get rid of air. Pour off most of the acid, and fill with fresh "boiled-out" acid. Insert the cork and capillary tube and arrange that the thread of acid is at the zero of the scale, or thereabouts, when placed in some calcium chloride solution warmed to about 80°C . in a beaker.

Warm the solution slowly on a sand bath, note the temperature at intervals, and the position of the thread of acid. When the transition takes place the expansion is greater. Plot the increase in volume per half degree rise in temperature and determine the transition point. (Theory, § 148.)

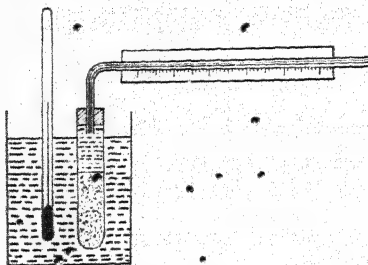


Fig. 125.—Dilatometer.

Experiment 27.—To determine the dissociation pressure of copper sulphate hydrates.

Obtain a tensimeter and place in one of the bulbs, copper sulphate pentahydrate which has been allowed to stand for a short time in a desiccator. This ensures that a small amount of trihydrate will be present. Carry out the experiment as described in § 148.

Experiment 28.—To study the mutual solubility of benzene, water and acetic acid.

Have two burettes, one filled with water, and the other with glacial acetic acid. Put 5 c.c. of benzene in a conical flask provided with a cork, add 1 c.c. of water, and run in glacial acetic acid until a clear solution is obtained on shaking. Note the volume required. This gives one composition for the mutual solubility. Add another 2 c.c. of water to the mixture, and then add more acetic acid until on shaking the solution is clear. Repeat with other concentrations. Plot the data on a triangular diagram. Since these experiments are carried out at constant temperature, the isothermal diagram is all that is required. (Theory, § 222.)

QUESTIONS ON CHAPTER XI

- (1) What do you understand by the terms "phase", "component", "degree of freedom", "equilibrium"? What is the Phase Rule? Give one example of its application.
- (2) What is the explanation of efflorescence and deliquescence?
- (3) What do you mean by a triple point? What triple points are to be observed in the sulphur system?
- (4) Draw a sketch and explain the principal features of the freezing point diagram for a mixture of two metals which do not form solid solutions. How is the diagram modified if a chemical compound is formed?
- (5) How may the Phase Rule be applied to a double salt and its solution in water? What type of diagram would you expect?
- (6) From the Phase Rule diagram for sulphur answer the following

questions: (a) is monoclinic sulphur more dense than rhombic sulphur? (b) is rhombic sulphur more dense than liquid sulphur? (c) is monoclinic sulphur more dense than liquid sulphur? Give reasons.

CHAPTER XII

SUGGESTIONS FOR PRACTICAL WORK

Experiment 29.—To study the system phenol-water.

Prepare sealed tubes containing the following amounts of phenol and water (approx.):—

	Phenol, gms.	Water gms.
I	0.6	4.4
II	1.0	4.0
III	1.5	3.5
IV	2.0	3.0
V	2.5	2.5
VI	3.0	2.0

Take the first tube, place it in a beaker of water of which the temperature (observed) is gradually raised. Shake, and note the temperature when the turbidity suddenly disappears. Note also the temperature at which the two layers appear, once more on cooling. Repeat these with the other tubes, taking in every case the mean of the temperatures of appearance and disappearance of the turbidity as the temperature at which complete miscibility occurs. Plot the temperatures against the concentrations, expressed as percentages. The maximum of the curve is the critical solution temperature. (Theory, § 244.)

Experiment 30.—To determine the solubility of ammonia in water and in methyl alcohol.

Use the method described in § 229. Generate the ammonia by warming the concentrated solution.

Experiment 31.—To determine the solubility of oxalic acid in water.

Adjust a thermostat for 25° C., and carry out the experiment as described in § 256. Estimate the oxalic acid by means of standard permanganate. It is an interesting experiment to determine also the solubility of oxalic acid in N/10 sulphuric acid. Explain the result (Chapter XV).

Experiment 32.—To determine the molecular weight of nitrobenzene by steam distillation.

Full instructions are given in § 254. Instead of nitrobenzene, chlorobenzene may be used satisfactorily.

Experiment 33.—To verify the extraction formula with succinic acid and ether.

Try 200 c.c. ether, first all together, and then in five lots of 40 c.c., and see which is the more effective. The experiment is not altogether satisfactory owing to the solubility of ether in water.

The experiment may also be carried out with bromine water and carbon tetrachloride.

QUESTIONS ON CHAPTER XII

(1) State Henry's Law. How far does it explain accurately the equilibrium between a gas and a solvent?

(2) How would you attempt to verify Dalton's Law of Partial Pressures? How may this law be deduced on the basis of the kinetic theory?

(3) Discuss the absorption of hydrogen by palladium.

(4) What are the characteristics of the solubility curves of (a) sodium sulphate in water, (b) phenol in water, (c) nicotine in water?

(5) Give the theory of fractional distillation.

(6) How may the molecular weight of a substance volatile in steam be obtained from a steam distillation experiment? What are the conditions that this experiment should give an accurate result?

(7) Deduce the general equation for extraction of a solid from solution by means of a liquid immiscible with the original solvent, with n extractions of v c.c. each.

(8) How would you distinguish between a solid solution and a solid chemical compound?

(9) In an investigation of the system anthracene-phenanthrene, Bradley and Marsh (*J. C. S.*, 1933, 650) obtained the following data:—

Per cent. anthracene	} by		0.56	2.30	3.13	5.06	5.82	9.54	11.7	13.3
Per cent. phenanthrene	} wt.		99.44	97.70	96.87	94.94	94.18	90.46	88.3	86.7
F.p., °C.			98.3	101.2	102.6	106.2	106.8	114.8	119.2	120.2
M.p., °C.			97.8	99.2	100.0	101.4	102.0	105.0	107.2	107.6
Per cent. anthracene by wt.	20.5	27.1	28.9	36.4	44.4	58.5	72.3	81.2	94.3	100.0
Per cent. Phenanthrene by wt.	79.5	72.9	71.1	63.4	55.6	41.5	27.7	18.8	5.68	0.00
F.p., °C.	134.0	145.4	147.8	159.4	170.0	186.4	199.2	204.8	213.2	218.0
R.p., °C.	113.5	118.2	120.8	126.2	133.2	147.8	170.0	182.2	207.6	218.0

Draw the liquids-solidus curves, and discuss them. Also, find the melting point of pure phenanthrene.

CHAPTER XIII

SUGGESTIONS FOR PRACTICAL WORK

Experiment 34.—Determine the molecular weight of urea by the vapour pressure method.

Fit up the apparatus as described in § 281. The dynamical method is to be used. Aspirate air through the apparatus slowly for about six hours.

Experiment 35.—Determine the molecular weight of urea in water by the freezing point method.

Use the method described in § 288. Rast's method should also be tried, using naphthalene in camphor.

Also show that potassium chloride in water gives anomalous results.

Experiment 36.—Determine the molecular weight of cane-sugar in water using the Landsberger method.

Details for all these experiments will be found in the text, and the student is advised also to try several others which will be found in the text-books of Practical Physical Chemistry, such as that by Sherwood Taylor, or by Findlay.

QUESTIONS ON CHAPTER XIII

(1) Describe a method of finding the molecular weight of a substance in solution.

When 0.25 gm. of a substance was dissolved in 100 gms. of water, the freezing point of the latter was lowered by 0.43°C . Find the molecular weight of the substance (molecular depression for water = 18.5°C).

(2) What methods are available for the determination of the molecular weight of (a) a gas, (b) a non-volatile electrolyte? Describe in detail one method for the latter class.

(3) Write an essay on the properties of dilute solutions.

(4) Show how the osmotic pressure of a solution is connected with the elevation of the boiling point.

(5) The boiling point of acetone is 56.38°C . A solution of 0.564 gm. of a compound in 8.6 gms. of acetone boiled at 56.75°C . What was the molecular weight of the compound? (Molecular elevation for acetone = 16.7°C .)

(6) How many observations of the vapour pressure of a solution be used to give information concerning the molecular weight of the substance dissolved?

(7) How are the latent heats of evaporation and fusion of a substance connected with the molecular elevation and depression respectively?

(8) The following results were obtained by Morse in experiments on the osmotic pressure of mannitol ($\text{C}_6\text{H}_{14}\text{O}_6$):—

Grams Mannitol in 100 gms. Water.	Osmotic Pressure, 10°C .	Osmotic Pressure, 40°C .
1.82	2.314 atm.	2.557 atm.
3.64	4.609 "	5.107 "
5.46	6.940 "	7.664 "
7.28	9.209 "	10.216 "

Show that these data agree with the Laws of Osmotic Pressure.

(9) Raoult found that a solution of 11.346 gms. of turpentine in 100 gms. of ether, $(\text{C}_2\text{H}_5)_2\text{O}$, had a vapour pressure of 360.1 mm. At the temperature of the experiment, the vapour pressure of pure ether was 383 mm. Calculate the molecular weight of turpentine.

(10) Will and Bredig (1889), using the dynamic method of determining the vapour pressure lowering of alcoholic solutions, found the following results:—

Substance.	Weight dissolved in 30 gms. alcohol. Gms.	b_1 . Gms.	b_2 . Gms.
Nitrobenzene	4.1	2.034	0.0884
Benzoic acid	4.28	1.8315	0.0731
Acetamide	5.04	0.6073	0.0525
Atropine	5.05	1.467	0.027
Vanillin	2.4	1.6895	0.0312

b_1 is the loss in weight of the set of bulbs containing the solution, and b_2 is the loss in weight of the bulbs containing alcohol. Calculate the molecular weights of these substances from the above data.

(11) Beckmann (1890) found the molecular weight of iodine as follows: 1.065 gms. of iodine were dissolved in 30.14 gms. of ether. The boiling point of the ether was raised by 0.296°C . The molecular weight of ether is 74, and the molecular elevation constant 21.1°C . Calculate the molecular weight of iodine.

(12) Andrews found the heat of vaporisation of 1 gm. of carbon disulphide to be 86.72 cal. Its boiling point is 46°C . Calculate the molecular elevation constant.

Beckmann found that 1.4475 gms. of white phosphorus dissolved in 54.65 gms. carbon disulphide raised the boiling point by 0.486°C . Calculate the molecular weight of white phosphorus.

(13) Pirsch found that 0.685 milligrams of anthraquinone dissolved in 8.943 milligrams of camphorquinone lowered the melting point of the latter by 16.6°C . If the molecular depression for camphorquinone is 457°C ., calculate the molecular weight of anthraquinone.

(14) 0.806 milligrams of naphthalene (C_{10}H_8), when dissolved in 9.930 milligrams of bornylamine, produced a depression of the freezing point of 32.5°C . Calculate the molecular depression for bornylamine.

(15) In determining the molecular weights of the alkaloids caffeine and morphine, Pirsch obtained the following results:—

Solvent — Bornylamine. $K = 406^{\circ}\text{C}$.

	Wt. of Solute. Mgms.	Wt. of Solvent. Mgms.	Depression of Freezing point. $^{\circ}\text{C}$.
Caffeine . . .	0.568	7.132	16.1
Morphine . . .	0.876	10.624	11.6

Calculate the molecular weights of these substances. The theoretical values are: caffeine 212, morphine 303.

(16) H. J. S. King, in research on amines, found the apparent molecular weight of diamminocupric acetate by the boiling point method. 0.3998 gm. of the salt was dissolved in 21.05 gms. of anhydrous alcohol. The boiling point was raised by 0.035°C . The molecular elevation for alcohol is 11.5°C . Calculate the apparent molecular weight of the salt.

(17) The molecular weight of selenium oxychloride, SeOCl_2 , in dry benzene, was determined by Henley and Sugden (*J. C. S.*, 1929, 1064), using the freezing point method. The following results were obtained:—

Concn. (gms. per 100 gms. of Benzene).	Depression, $^{\circ}\text{C}$.
1.925	0.578 ^{0.578}
4.713	1.445
6.06	1.641

Calculate the molecular weight of selenium oxychloride from each of these observations. To what conclusion do they lead concerning the molecular condition of selenium oxychloride in benzene solution?

CHAPTER XIV

SUGGESTIONS FOR PRACTICAL WORK

Experiment 37.—Determine the conductivity of a solution of copper sulphate, and calculate its molecular and equivalent conductivities (§ 298).

Experiment 38.—Determine the variation of equivalent conductivity of copper sulphate with temperature.

Repeat the above experiment, placing the cell in baths of various temperatures. Plot the equivalent conductivity against temperature.

Experiment 39.—Determine the transport numbers of the silver and nitrate ions (§ 307).

QUESTIONS ON CHAPTER XIV

- (1) State Faraday's Laws of Electrolysis. How may they be verified?
- (2) Explain what takes place when an electric current is passed successively through solutions of copper sulphate, silver nitrate, lead acetate and sodium chloride, the electrodes being of platinum. What is the relationship between the quantities of substances liberated?
- (3) What is meant by the term "degree of dissociation"? How may it be determined?
- (4) How is it possible to determine the equivalent conductivity of acetic acid at infinite dilution?
- (5) In what way does the electrical conductivity of a solution vary with dilution? How can the variation be explained?
- (6) What is meant by the term "ionic mobility"? How may the ionic mobilities be determined, and of what use are they?
- (7) How may the actual mobility of the hydrogen ion be demonstrated?
- (8) When an electric current is passed through a solution of zinc chloride between carbon electrodes, a certain minimum potential is necessary to effect decomposition. Why is this?
- (9) Calculate the osmotic pressure of an $M/10$ solution of urea, $\text{CO}(\text{NH}_2)_2$ at 0°C . Why is it that the osmotic pressure of $M/10$ solution of potassium chloride is almost twice as great as this?
- (10) A 1 per cent. solution of sodium chloride freezes at -0.604°C . The molecular depression of water is 18.5° (100 gms.). Calculate the degree of dissociation of the sodium chloride.
- (11) What is meant by the transport number of an ion? How may it be determined?
In a transport number experiment a solution of silver nitrate containing 0.0074 gm. per gram of water was used. During the experiment 0.0785 gm. of silver was deposited in a silver voltameter placed in series with the transport apparatus. After the experiment, 25 gms. of the anode solution contained 0.2553 gm. of silver nitrate. Find the transport numbers of the silver and nitrate ions. The electrodes were of silver.
- (12) The velocity of migration of the silver ion 18°C . is 0.000577 cm. per sec., and that of the nitrate ion 0.000630 cm. per sec. What is the specific conductance of a 0.1 M silver nitrate solution if the van't Hoff i factor is 1.5? All observations are made at the same temperature.
- (13) Discuss the results of conductivity work in non-aqueous solutions.
- (14) In what ways does a knowledge of the electrical conductivity of an alloy give information as to its nature?

(15) Nernst and Loeb, in determining the transport numbers of the silver and nitrate ions, found the following results: Before the experiment, 1 gm. of the anode solution contained 0.001788 gm. of silver nitrate. After the experiment 20.09 gms. of solution taken from the anode compartment contained 0.06227 gm. of silver nitrate. 0.0322 gm. of silver was deposited in a voltameter placed in the circuit. Calculate the transport numbers of the silver and nitrate ions.

(16) The osmotic pressures of solutions of potassium nitrate, at 15° C., are given in the following tables:—

Conc. (%)	Pressure (cms.)
0.80	130.4
1.43	218.5
3.3	436.8

Calculate the apparent molecular weight of potassium nitrate from each of these observations, and explain the results.

CHAPTER XV

SUGGESTIONS FOR PRACTICAL WORK

Experiment 40.—Carry out an electrometric titration of sodium hydroxide by hydrochloric acid. (See Chapter XIV.)

Experiment 41.—Determine the degree of hydrolysis of aniline hydrochloride by the distribution method (§ 328).

QUESTIONS ON CHAPTER XV

- (1) In what ways does the failure of Ostwald's Dilution Law to explain the behaviour of strong electrolytes necessitate revision of Arrhenius' hypothesis?
- (2) What is meant by the term "degree of hydrolysis"? How would you determine the degree of hydrolysis of aniline hydrochloride?
- (3) What methods are available for the quantitative determination of hydrolysis?
- (4) How may the ionic product for water be determined? Why is this an important figure?
- (5) What do you mean by the term "solubility product"? Show how the concept can be used to explain many of the processes of qualitative analysis.
- (6) How would you attempt to verify the constancy of the solubility product for silver chloride?
- (7) Calculate the pH at 25° C. of mixtures of
 - (a) 164 c.c. N/5 acetic acid and 36 c.c. N/5 sodium acetate.
 - (b) 59 c.c. N/5 acetic acid and 141 c.c. N/5 sodium acetate.
 - (c) 9 c.c. N/5 acetic acid and 191 c.c. N/5 sodium acetate.
- (8) The dissociation constant of acetic acid at 25° C. is 1.8×10^{-5} . The variation of the dissociation constants of acetic acid (K_a) and ammonia (K_b), with temperature are given in the following Table:—

Temp., °C.	18°	100°	156°
K_a	1.72×10^{-5}	1.35×10^{-5}	6.28×10^{-6}
K_b	1.83×10^{-5}	1.11×10^{-5}	5.36×10^{-6}

Calculate the degree of hydrolysis of $M/10$ solutions of ammonium acetate at 18° C., 100° C. and 156° C. What effect has temperature on the degree of hydrolysis?

(9) Williams and Soper (*J.C.S.*, 1930, 2469) determined the hydrolysis constant of *o*-chloroaniline hydrochloride by the distribution method. The distribution coefficient of the free amine between water and benzene was first determined. 1,000 c.c. of water were used, and 60 c.c. benzene (counted as 59 c.c. to make up for solution of benzene in the aqueous layer). The following were the results:—

Wt. of R. NH_2 put in, gms.	Wt. of R. NH_2 in 59 c.c. Benzene, gms.
2.6128	2.293
3.0647	2.683
1.3380	1.166
1.2000	1.053

Calculate the distribution coefficient and obtain its mean value. In the second part of the experiment unequal amounts of hydrochloric acid and the amine were mixed in the aqueous layer (1,000 c.c.) and shaken with 60 c.c. benzene. c_1 and c_2 are the total initial molar concentrations of hydrogen chloride and the amine respectively.

c_1	c_2	Wt. of RNH_2Cl from 50 c.c. Benzene, gms.
0.01206	0.01122	0.9800
0.02671	0.02569	1.7694
0.02896	0.02281	1.5084
0.01853	0.01534	1.1706

Calculate the hydrolysis constant K_h from each of these readings, and find its mean value.

Assuming that K_w at the temperature of the experiment (25° C.) is 1.005×10^{-14} , calculate the dissociation constant of *o*-chloroaniline hydroxide.

(10) How far is it true to say that the strength of an acid is determined by the hydrogen ion concentration of its solution?

(11) By what methods may hydrogen ion concentration be determined? Indicate the importance of hydrogen ion concentration values.

(12) Define the terms "acid" and "base". Criticise the usually accepted definitions.

(13) Discuss the neutralisation of an acid by a base.

QUESTIONS ON CHAPTER XVI

- (1) Give an account of the working of a voltaic cell.
- (2) What physico-chemical information can be derived from measurements of the e.m.f. of cells?
- (3) How would you determine the solubility product of silver chloride?
- (4) Of what interest is a table of oxidation-reduction potentials?

CHAPTER XVII

SUGGESTIONS FOR PRACTICAL WORK

Experiment 42.—Prepare some colloidal solutions according to the instructions given in this chapter.

Experiment 43.—Compare the effects of solutions of potassium chloride, calcium chloride, and aluminium chloride in coagulating an arsenic sulphide sol.

Make up some arsenic sulphide sol and place 10 c.c. of it in each of nine clean test-tubes. Add to the tubes the following mixtures:—

- (a) 5 c.c. 0.1 M KCl + 5 c.c. water.
- (b) 1 c.c. 2.0 M KCl + 9 c.c. water.
- (c) 2 c.c. 2.0 M KCl + 8 c.c. water.
- (d) 0.5 c.c. 0.1 M CaCl_2 + 9.5 c.c. water.
- (e) 2.0 c.c. 0.1 M CaCl_2 + 8.0 c.c. water.
- (f) 4.0 c.c. 0.1 M CaCl_2 + 6.0 c.c. water.
- (g) 0.5 c.c. 0.001 M AlCl_3 + 9.5 c.c. water.
- (h) 2.0 c.c. 0.001 M AlCl_3 + 8.0 c.c. water.
- (i) 4.0 c.c. 0.001 M AlCl_3 + 6.0 c.c. water.

Find the least concentrations of the various salts necessary for precipitation. Compare with theory (§ 357). (The above figures are taken from Sherwood Taylor, "Elementary Practical Physical Chemistry". Oxford University Press.)

QUESTIONS ON CHAPTER XVII

- (1) Describe the preparation of a colloidal solution of arsenic sulphide. What is the effect of the addition of electrolytes to this sol?
- (2) Classify the various types of colloidal solution. What methods indicate the heterogeneous nature of colloidal solutions?
- (3) Classify the various methods of producing colloidal solutions and give examples of each.
- (4) What is meant by the gold number of a colloid? How would you determine it?
- (5) State the Hardy-Schulze Law, and discuss it.
- (6) How may the Avogadro number be determined from a study of colloidal particles?
- (7) How may the sign of the charge on a colloidal particle be determined? Discuss the part played by the charge in determining the stability of a colloid.
- (8) Discuss the applications of colloid chemistry to qualitative and quantitative analysis.

- (9) What is the essential difference between the extraction of iodine from a solution by means of chloroform and that by finely divided charcoal?
- (10) Give an account of the adsorption of a gas on a solid surface.
- (11) Write an essay on surface films at an air-water interface.

CHAPTER XVIII

SUGGESTIONS FOR PRACTICAL WORK

Experiment 44.—To determine the effect of a catalyst on the rate of a chemical reaction.

A good reaction to study is that recommended by Sherwood Taylor, "Elementary Practical Physical Chemistry", viz.,



This reaction is not termolecular, as indicated by the equation, but is bimolecular. It is catalysed by cupric or ferrous ions. The rate of the reaction is conveniently studied by taking out portions from time to time and titrating against standard thiosulphate. This gives the amount of iodine liberated.

Make up a solution of potassium persulphate 0.05 molar, and one of potassium iodide 0.1 molar. The reaction should be carried out at room temperature. Mix 50 c.c. of the persulphate, and 50 c.c. of the iodide, and 20 c.c. of water. Note the time of mixing, and withdraw 10 c.c. at a time at intervals of five minutes and titrate with *N*/50 thiosulphate. Note the time of removal as that when the first drop of thiosulphate is added. See whether the results fit the bimolecular equation, and calculate a value for the velocity constant.

Now repeat the experiment using instead of the 20 c.c. of water 20 c.c. of 0.5 per cent. solution of copper sulphate.

In calculating the amount of iodine, calculate the amount formed by the action of the copper sulphate on the iodide and subtract that from the amount titrated.

See whether the bimolecular equation still holds, and calculate the new velocity constant.

SUGGESTIONS FOR FURTHER PRACTICAL WORK

Study the effect of the following substances as catalysts on the mutarotation of glucose:

- (1) *N* Potassium chloride.
- (2) *N*/10 Hydrochloric acid.
- (3) *N* Sodium acetate, approximately neutralised by addition of *N*/20 acetic acid.

QUESTIONS ON CHAPTER XVIII

- (1) What is meant by the term "catalysis"? What criteria of catalytic behaviour have been laid down? Discuss their applicability.
- (2) Write an account of water as a catalyst.
- (3) Discuss the work on catalysis by hydrogen ions and by neutral salts.
- (4) What mechanism can be ascribed to heterogeneous catalysis?

QUESTIONS ON CHAPTER XIX

- (1) What laws concern the absorption and reflection of light? Discuss their accuracy.
- (2) Indicate briefly how a study of absorption spectra can furnish information concerning the structure of compounds.
- (3) Describe any one photochemical system with which you are acquainted.
- (4) Write an essay on the application of the quantum theory to photochemical processes.
- (5) Write notes on fluorescence, phosphorescence, and chemiluminescence, giving some account of their explanation.
- (6) How do you account for the fact that in the combination of hydrogen and chlorine by exposure to ultra-violet light more than 10^5 molecules are formed per quantum of energy absorbed?

QUESTIONS ON CHAPTER XX

- (1) Show in what ways a knowledge of the dielectric constant of a substance may throw light on its constitution.
- (2) Water has a dipole moment of 1.98. What does this statement mean, and what does it imply?
- (3) Describe the various types of spectra emitted by atoms and molecules. Explain the differences between them.
- (4) Show how the structure of a simple molecule can be investigated by a study of spectra.

ANSWERS TO NUMERICAL EXAMPLES

Chapter I.

9. (a) It is a metal; hence Dulong and Petit's Law holds.
(b) Rough value for atomic weight is 53.79.
(c) Equivalent is 18.61; hence valency is 3, and correct atomic weight is 55.83.
(d) Equivalent is 27.92; hence valency is 2, and correct atomic weight is 55.84.
10. 126.918; 126.920; 126.917.
11. 138.923; 138.909; 138.931.
12. 176.1.
13. 123.7.
14. Ag_2S : $2\text{Ag} = 1.158617$; 1.148620 ; 1.148617 ; 1.148622 .
At. weight = 32.066; 32.066; 32.066; 32.067. S. 87
15. Common, 207.222; 207.209.
Kolm, 205.990; 205.999.
Uraninite, 206.194; 206.196.

Chapter V.

1. -102,380 gm.-cals.
4. -323,300 gm.-cals.
8. -18,300 gm.-cals.
9. Constant pressure:—Ethane, -23,550 gm.-cals. Ethylene, 7,830 gm.-cals. Acetylene, 52,860 gm.-cals.
Constant volume:—Ethane, -22,390 gm.-cals. Ethylene, 8,410 gm.-cals. Acetylene, 52,860 gm.-cals.

Chapter VII.

3. 27.880; 11.88.
7. (a) Ethylene, 28.051; (b) carbon dioxide, 44.014; (c) nitrous oxide, 44.016; (d) sulphur dioxide, 64.004; (e) dimethyl ether, 64.003.
Atomic weights: Carbon (from a), 12.010; (from b), 12.014; (from e), 11.98; Nitrogen (from c), 14.008; Sulphur (from d) 32.00.

Chapter IX.

8. 630.
9. Ethylene, 101.2; Acetone, 160.2; Nitrosyl chloride, 110.0.
10. SF_6 , 143.1; SeF_6 , 159.8; TeF_6 , 173.4.
11. The constant obtained by Dunstan's equation is 116.3. Hence the liquid is probably associated.
12. The value of the constant from Dunstan's equation is about 200, which would indicate that the liquid is probably associated. It should be noted, however, that nitrobenzene often behaves in an anomalous manner, and hence it is unwise to place too much reliance on this figure.

Chapter X.

10. The reaction is unimolecular.
11. The reaction is unimolecular ($k = 0.01148$).
13. 24,700 gm.-cals.
14. 58,500 gm.-cals.
15. The reaction is bimolecular ($k \times 10^3 = 2.85, 2.88, 2.91, 2.92$).
16. The reaction is bimolecular; using the equation

$$k = \frac{1}{(a-b)t} \log_e \frac{b(a-x)}{a(b-x)}, k \times 10^4 = 4.28, 4.32, 4.33, 4.39, 4.40.$$

Chapter XII.

9. 97.3°C .

Chapter XIII.

1. 10.75.
5. 296.
9. 132.
10. Nitrobenzene, 122; Benzoic acid, 107; Acetamide, 58; Atropine, 275; Vanillin, 130.
11. 251.9.
12. 29.56°C ; 161.1.
13. 210.9.
14. 101.4.
15. Caffeine, 207; morphine, 289.
16. 624.
17. 170.5; 179.5; 189.1.

Chapter XIV.

- a. 2.241 atmos. at 0°C . (using $R = 0.0821$ litre-atmos. per degree).
10. 0.91.
11. Ag^+ , 0.431; NO_3 , 0.569.
12. 0.005825 mhos.
15. Ag^+ , 0.478; NO_3 , 0.522.
16. 110.24; 117.6; 135.7.

Chapter XV.

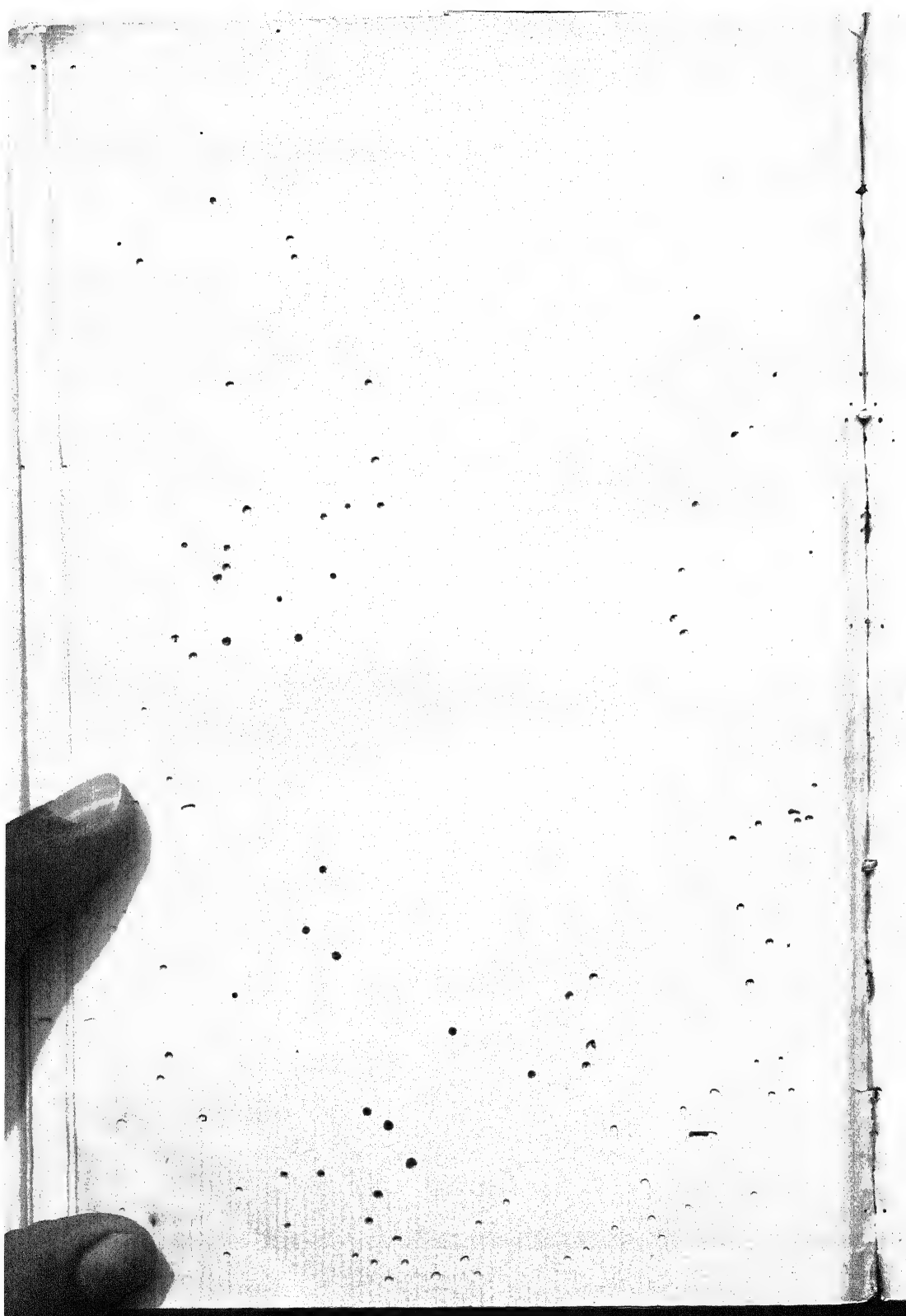
7. (a) 4.05; (b) 5.16; (c) 6.20.
8. $K_h = 3.177 \times 10^{-5}$; 6.674×10^{-5} ; 3.74×10^{-4} . The degree of hydrolysis, h , corresponding to the above hydrolysis constants is 5.64×10^{-3} ; 8.17×10^{-3} ; 1.93×10^{-2} .
The values of h given, have been calculated by neglecting h in comparison with unity.
9. Distribution coefficient:—121, 119, 115, 121. Mean, 119.
 $K_h \times 10^3$:—2.83, 2.53, 2.76, 2.70. Mean, 2.71.
 $K_h \times 10^{11}$:—0.371.

ATOMIC WEIGHTS, 1949

Taken by kind permission from the *Journal of the Chemical Society*.

Atomic weights in brackets denote the mass number of the most stable known isotope.

Atomic number	Name	Sym- bol	Atomic weight	Atomic number	Name	Sym- bol	Atomic weight
1	Hydrogen	H	1.0080	49	Indium	In	114.76
2	Helium	He	4.003	50	Tin	Sn	118.70
3	Lithium	Li	6.940	51	Antimony	Sb	121.76
4	Beryllium	Be	9.013	52	Tellurium	Te	127.61
5	Boron	B	10.82	53	Iodine	I	126.92
6	Carbon	C	12.010	54	Xenon	Xe	131.3
7	Nitrogen	N	14.008	55	Cæsium	Cs	132.91
8	Oxygen	O	16.0000	56	Barium	Ba	137.36
9	Fluorine	F	19.00	57	Lanthanum	La	138.92
10	Neon	Ne	20.183	58	Cerium	Ce	140.13
11	Sodium	Na	22.997	59	Praseodymium	Pr	140.92
12	Magnesium	Mg	24.32	60	Neodymium	Nd	144.27
13	Aluminium	Al	26.97	61	Promethium	Pm	[147]
14	Silicon	Si	28.06	62	Samarium	Sm	150.43
15	Phosphorus	P	30.98	63	Europium	Eu	152.0
16	Sulphur	S	32.066	64	Gadolinium	Gd	155.1
17	Chlorine	Cl	35.457	65	Terbium	Tb	159.2
18	Argon	A	39.944	66	Dysprosium	Dy	132.46
19	Potassium	K	39.096	67	Holmium	Ho	164.94
20	Calcium	Ca	40.08	68	Erbium	Er	167.2
21	Scandium	Sc	45.10	69	Thulium	Tm	169.4
22	Titanium	Ti	47.90	70	Ytterbium	Yb	173.04
23	Vanadium	V	50.95	71	Lutecium	Lu	174.96
24	Chromium	Cr	52.01	72	Hafnium	Hf	178.6
25	Manganese	Mn	54.93	73	Tantalum	Ta	180.881
26	Iron	Fe	55.85	74	Tungsten	W	183.92
27	Cobalt	Co	58.94	75	Rhenium	Re	186.31
28	Nickel	Ni	58.69	76	Osmium	Os	190.2
29	Copper	Cu	63.54	77	Iridium	Ir	193.1
30	Zinc	Zn	65.38	78	Platinum	Pt	195.23
31	Gallium	Ga	69.72	79	Gold	Au	197.2
32	Germanium	Ge	72.60	80	Mercury	Hg	200.61
33	Arsenic	As	74.91	81	Thallium	Tl	204.39
34	Selenium	Se	78.96	82	Lead	Pb	207.21
35	Bromine	Br	79.916	83	Bismuth	Bi	209.00
36	Krypton	Kr	83.7	84	Polonium	Po	210
37	Rubidium	Rb	85.48	85	Astatine	At	[210]
38	Strontium	Sr	87.63	86	Radon	Rn	222
39	Yttrium	Y	88.92	87	Francium	Fr	[223]
40	Zirconium	Zr	91.22	88	Radium	Ra	226.05
41	Niobium	Nb	92.91	89	Actinium	Ac	—
	(Columbium)	(Cb)		90	Thorium	Th	232.12
42	Molybdenum	Mo	95.95	91	Protoactinium	Pa	231
43	Technetium	Tc	[99]	92	Uranium	U	238.07
44	Ruthenium	Ru	101.7	93	Neptunium	Np	[237]
45	Rhodium	Rh	102.91	94	Plutonium	Pv	[239]
46	Palladium	Pd	106.7	95	Americium	Am	[241]
47	Silver	Ag	107.880	96	Curium	Cm	[242]
48	Cadmium	Cd	112.41				



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The names of persons are given in *italics*, except where the name is an integral part of the reference. The numbers refer to pages.

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